

CANADIAN JOURNAL OF RESEARCH

VOLUME 14

APRIL, 1936

NUMBER 4

CONTENTS

SEC. A.—PHYSICAL SCIENCES

	Page
The Scotoscopic Effect in Vision— <i>Frank Allen and M. J. Oretzki</i> -	71
Determination of the Natural Wave-length of an Antenna by the Reactance Method— <i>George Sinclair</i> - - - - -	87

SEC. B.—CHEMICAL SCIENCES

Studies on Lignin and Related Compounds. XXII. Fractiona- tion of Methanol Lignin— <i>Jack Compton, Margaret Greig and</i> <i>Harold Hibbert</i> - - - - -	115
The Solubility of Carbon Dioxide in Aqueous Solutions Con- taining Alcohols and Sugars— <i>H. A. Showalter and J. B.</i> <i>Ferguson</i> - - - - -	120
Studies of Carbon Black. II. The Channel Process—Production from the Natural Gas of Turner Valley, Alberta— <i>L. M. Pid-</i> <i>geon</i> - - - - -	127

NATIONAL RESEARCH COUNCIL
OTTAWA, CANADA

Publications and Subscriptions

The Canadian Journal of Research is issued monthly in four sections, as follows;

- A. Physical Sciences
- B. Chemical Sciences
- C. Botanical Sciences
- D. Zoological Sciences

For the present, Sections A and B are issued under a single cover, as also are Sections C and D, with separate pagination of the four sections, to permit separate binding, if desired.

Subscription rates, postage paid to any part of the world (effective 1 April, 1939), are as follows:

	<i>Annual</i>	<i>Single Copy</i>
A and B	\$ 2.50	\$ 0.50
C and D	2.50	0.50
Four sections, complete	4.00	—

The Canadian Journal of Research is published by the National Research Council of Canada under authority of the Chairman of the Committee of the Privy Council on Scientific and Industrial Research. All correspondence should be addressed:

National Research Council, Ottawa, Canada.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 14, SEC. A.

APRIL, 1936

NUMBER 4

THE SCOTOSCOPIC EFFECT IN VISION¹

BY FRANK ALLEN² AND M. J. ORETZKI³

Abstract

When an illuminated wall of a room is observed by the two eyes, before one of which a tube with opaque sides is held, the patch of the wall seen through the tube appears brighter and nearer to the eye than the rest of the surface appears to the other eye. This may be termed the photoscopic effect.

If the side of the tube is translucent and brightly illuminated, the patch of the wall will appear darker than the remainder of the surface. When a sectored disc is rotated at a certain critical speed in front of the tube, the patch of the wall seen through it appears intensely black. This appearance of blackness is called the scotoscopic effect.

The critical speed of rotation of the disc at which the scotoscopic effect appears, differs for the fovea, macula and periphery of the retina. The respective areas of those regions are quite sharply distinguished from one another.

In a number of investigations (1, 2, 3) on color vision which were conducted by one of the writers, it was shown that underlying and influencing all visual activities are the physiological processes of inhibition and facilitation by which the sensitivity of the receptors, or of the corresponding central organ, is respectively depressed or enhanced. It has also been shown that stimulation of one area of a retina with light produces by these processes corresponding changes in the responsiveness of adjacent areas whereby their excitability is lowered or raised. To this reciprocal action of stimulated areas upon each other are due the phenomena of simultaneous contrast in which adjacent patches of different colors, or of light and dark shades, are modified in appearance. Contrast, or simultaneous induction as it is also termed, may therefore be regarded as the result of the operation of the principle of reciprocal innervation (8) in the visual neural apparatus. This principle implies more than the mutual influence of parts of the organism upon each other. In the case of antagonistic pairs of muscles, such as those of the arm, when the flexor muscle is contracted the antagonistic extensor muscle is proportionately relaxed. When the extensor in turn is contracted, the flexor is gradually relaxed. In the retina, also, the principle of contrast implies that the adjacent areas, on which the contrasting colors or lights appear, are modified in sensitivity to give differing conditions of excitability.

When one looks through an opaque tube with one eye, having the other eye open also, and directs the vision towards the wall of a room, it will be noticed that the area seen through the tube is much brighter than the rest of

¹ Manuscript received January 14, 1936.

Contribution from the Department of Physics, University of Manitoba, Winnipeg, Canada.

² Professor of Physics, University of Manitoba, Winnipeg.

³ Research student.

the wall as it appears to the other eye. For the most decided effect, the tube should be long, blackened on the inside, of small diameter, and directed so that only the light reflected from the wall enters it. The effect may also be readily obtained with a roll of common wrapping paper. Even the closed hand held to one eye will produce the same result. A friend of the writer, who had seen the phenomenon in the laboratory, made practical use of it in shooting by holding both closed hands to his eyes like an opera glass, and in this way he was able to distinguish flying ducks against the bright sky at unusually great distances, and so was the better prepared for them.

The function of the dark tube is to prevent light from reaching and stimulating the periphery of the retina; and the longer and narrower the tube, the greater is the area of the darkened periphery and the smaller is the illuminated central part. The pattern on the retina is therefore a bright central spot surrounded by a broad unilluminated area; or, a stimulated central portion in the midst of an unstimulated periphery. This photoscopic effect may be regarded as an extreme case of luminosity contrast. The remarkable enhancement of the brightness of the central spot seems, however, to be something more than simple luminosity contrast. Since the withdrawal of light from the periphery is accompanied by the enhancement of the central region, it is evident that stimulation of the periphery in normal vision exerts a constant inhibitory influence upon the excitability of the central retina by which the brightness of its visual responses is much reduced. If, then, the periphery is shielded from light, it no longer possesses inhibitory power upon the centre, and in consequence the light falling upon that region excites an enhanced sensation of brightness. The use of long, narrow and blackened tubes simply shields more completely greater areas of the periphery from light, and reduces the central stimulated area to the macula or even to the fovea with increasing power of response.

It is clear that, in the use of the telescope and microscope, the eye derives much of its visual power from the withdrawal of central inhibition by keeping the periphery dark through the use of blackened tubes.

This photoscopic effect was for some time a subject of much interested discussion in the writers' laboratory. Dr. H. A. Blair, who was then a research student, made some preliminary observations on the effect, and especially on the reverse effect of stimulating the periphery of the retina with fairly intense white light, whereby it was correctly anticipated that a darkening of the central field seen through the tube would be the result. The experiment was performed with a glass tube covered with a single layer of white translucent tissue paper which was brightly illuminated by an electric lamp.

It was found that a more pronounced darkening of the central field could be obtained by placing the covered glass tube on a stand on a table and directing it at a white screen, while in front of the far end of the tube was placed a disc with two opposite sectors of 90° each removed, and the two remaining sectors of the same size blackened. The tube was illuminated by electric lights suspended above it, and the eyes of the observer were shielded from their

direct rays. The white screen was illuminated also, though not so brightly as the tube. On looking through the tube when the disc was slowly rotated, there was observed a flickering effect as the open and closed sectors passed successively in front of the tube. When, by speeding up the motor, the critical frequency of flicker was reached, the flickering effect vanished and was replaced by an appearance of remarkably deep blackness. This is termed the scotoscopic effect.

These observations of Blair's were never completed, and, after he had received an appointment elsewhere, it was subsequently decided to investigate the phenomenon more fully with a different observer.

First Method of Investigation

In the present investigation several experimental arrangements of varying effectiveness were employed. The first apparatus consisted of a number of celluloid tubes, 12 in. long and from 1 to 2 in. in diameter, covered with a single layer of white tissue paper. They were held in a convenient position on a support and illuminated over their whole length by four 60-watt frosted Mazda lamps placed in a line parallel to the tube. In front of the tube at a distance of about two feet was placed a white screen, and near the end of the tube the disc was situated. Rotation was effected by a d-c. motor, the speed of which could be adjusted by means of a hand brake. At every fiftieth revolution of the armature, a speed counter attached to its shaft closed an electric chronograph circuit. Another chronograph circuit was closed every half-second by a clock. From these records the speed of the sectored disc could be computed and the critical frequency of flicker obtained.

In making observations, the right eye of the observer was placed so as to look through the tube and through an open sector of the disc at the white screen. The left eye was open and received the general illumination of the room. The disc was then rotated at a gradually increasing speed until the critical frequency of flicker was reached, at which point the circular patch of the screen observed through the tube became intensely black. The chronograph switch was then closed for four or five seconds and the speed of the disc recorded.

During the periods of observation in the entire investigation, care was taken to maintain the eyes in the normal condition of daylight adaptation. Observations were accordingly made only between the hours of 10 a.m. and 3 p.m. As in this climate the days are generally bright and clear, the daylight adaptation of the eyes may safely be assumed to have been sensibly constant. Though the observations were made in a room from which daylight was excluded, there was some diffused illumination from the lamps lighting the tube and screen. Between successive readings the observer rested his eyes from three to five minutes in an adjoining room illuminated by daylight, but he always refrained from looking at the bright windows.

The purpose of the investigation was to study the scotoscopic effect over gradually increasing areas of the retina. Knowing the length of the tube,

the area of the far end and the dimensions of the average eye given by Tscherning (9, chap. 2), the area of the retina illuminated chiefly by the light coming from the screen through the tube could be approximately computed.

In Table I are given five sets of measurements with tubes of eight different diameters, that is, for central retinal areas of eight different magnitudes. For graphical representation, it was found that by plotting logarithms of the

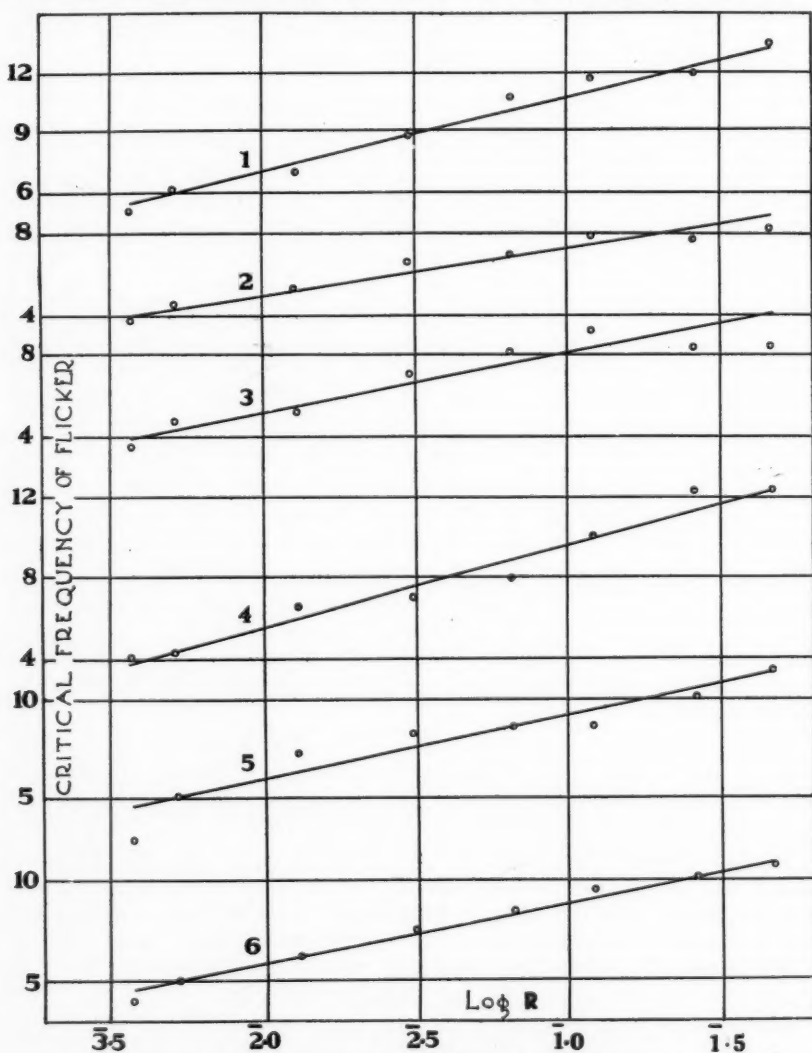


FIG. 1. Scotoscopic effect with increasing retinal areas.

areas as abscissas and critical frequencies of flicker as ordinates, fair approximations to straight lines were obtained which are shown in Fig. 1 in the graphs numbered from 1 to 5. Some of the readings, it will be seen, do not conform very well to the linear form of the graphs. This indicates that the method of

TABLE I*
CRITICAL FREQUENCY OF FLICKER

log <i>R</i>	Graph 1	Graph 2	Graph 3	Graph 4	Graph 5	Graph mean
3.568	5.12	3.64	3.50	4.12	2.94	3.86
3.708	6.20	4.54	4.76	4.26	5.13	4.98
2.114	7.05	5.26	5.08	6.45	7.20	6.21
2.491	8.69	6.66	6.97	6.90	8.16	7.47
2.821	10.81	6.97	8.00	7.84	8.45	8.41
1.141	11.76	7.89	9.11	10.00	8.51	9.45
1.423	11.93	7.78	8.19	12.20	10.00	10.02
1.673	13.33	8.10	8.33	12.30	11.32	10.68

*Fig. 1.

NOTE:—*R* is the area of retinal illumination in square inch measurement.

measurement is rather faulty. It is also evident that the central retina received some illumination from the walls of the tube. The mean values of the five sets of readings in Table I are plotted in Graph 6 of Fig. 1. Their conformity to the linear relation is very satisfactory.

The positive slope of the graphs indicates that as the logarithm of the central retinal area under stimulation increases, the critical frequency of flicker required to produce the scotoscopic effect increases also. The greater the critical frequency of flicker is, the shorter is the reciprocal quantity, that is, the duration of a flash of light through the open sector of the disc upon the eye, and also the shorter is the time during which it is cut off by a black sector. It is evident, therefore, that the responsiveness of the central retina increases with increasing areas of stimulation.

Second Method of Investigation

In the second set of experiments, instead of varying the diameters of tubes of the same length, a single tube of uniform diameter was used and its length varied. For this purpose the tube selected was 0.5 in. in diameter and 24 in. in length. It was numbered in 1 in. divisions for a distance of 20 in. from the far end, and in 0.5 in. divisions for the remaining distance. A reading was first taken, as already described, with a 24 in. tube. Immediately afterwards 1 in. was cut off, and, after the usual interval of rest, the second reading was made. In three sets of observations, from 11 to 13 different lengths of tube were employed, and the corresponding measurements are given in Table II, and plotted in Fig. 2 as Graphs 1, 2 and 3, in the same manner as before.

TABLE II*

log R	C.F.F. Graph 1	log R	C.F.F. Graph 2	log R	C.F.F. Graph 3
3.740	2.85	3.954	3.73	3.809	6.18
3.785	3.12	2.008	3.70	3.888	3.17
3.845	3.50	2.071	3.77	3.958	2.44
3.982	2.77	2.146	4.82	2.043	3.17
2.187	4.34	2.187	5.19	2.110	4.39
2.283	4.76	2.243	4.65	2.189	3.73
2.410	6.45	2.283	4.88	2.286	4.65
2.488	8.69	2.342	6.06	2.344	4.44
2.585	7.54	2.409	6.12	2.411	6.25
2.711	8.51	2.488	6.25	2.490	6.59
2.887	11.76	2.585	8.85	2.587	8.00
		2.710	7.50	2.712	9.52
		2.887	10.00		

* Fig. 2.

NOTE:— R is the area of retinal illumination (square inch).
C.F.F. is critical frequency of flicker.

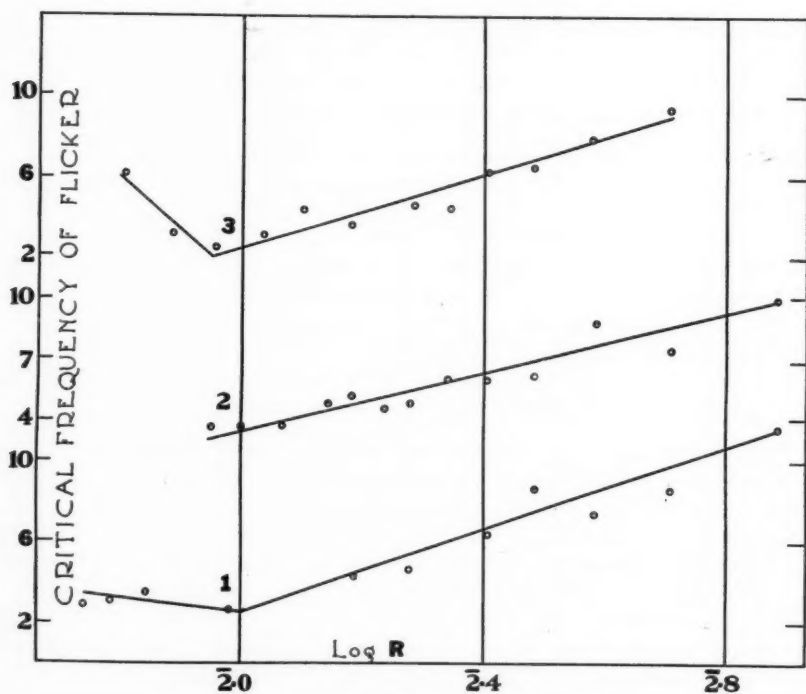


FIG. 2. Scotoscopic effect with increasing retinal areas.

The graphs again show that a linear relation exists between the logarithms of the areas stimulated and the critical frequencies of flicker at which the scotoscopic effect occurs. A new fact, however, emerges which indicates that the scotoscopic effect does not uniformly change with increasing retinal areas. For the two longer graphs are now seen to consist of two intersecting straight lines of opposite slopes. There appears to be, therefore, a certain critical area for which the scotoscopic effect is excited by the lowest value of the critical frequency of flicker; and for areas both smaller and larger than this, the effect occurs at higher values of the critical frequencies.

Further discussion of the significance of this interesting fact will be deferred until the next series of observations is considered. It may be remarked, however, that the straight lines on the left of the graphs represent the smaller areas of the retina, and those on the right, the larger areas involved. It is worthy of notice, moreover, that the scotoscopic effect is evoked at much lower values of the critical frequency of flicker, from about 2 to 12 impulses per second, than those found in experiments on the fusion of intermittent flashes of color from the spectrum, where the critical frequency ranges from 10 to 70 impulses per second.

Third Method of Investigation

Since much difficulty was experienced in fitting the tube of small diameter to the eye to prevent leakage of light around the outside of the tube, a third method of making observations was devised. A celluloid tube 3 in. in diameter was shaped at one end to fit closely the side of the head and round the right eye, and at the other to hold flat celluloid discs. The discs and tube were covered with white tissue paper. Each disc had a hole in the centre, varying from 0.25 to 2 in. in diameter, through which a patch of the illuminated screen could be observed. From the diameter of the hole in the disc, its distance from the eye and the dimensions of the normal eye, the illuminated area of the retina on which the scotoscopic effect occurred could be approximately computed. This arrangement was found to be highly satisfactory, and it was therefore used for the remainder of the work. With this method very small holes in the disc could be used, and correspondingly small areas of the retina, even less than of foveal size, could be intermittently stimulated.

The readings taken with this arrangement of apparatus are given in Table III, Columns 1, 2, and 3, and they are graphically shown in Fig. 3, in correspondingly numbered graphs. These graphs, while not coincident, are nevertheless in such good agreement, and represent so nearly similar conditions of visual adaptation and illumination, that a mean graph, No. 4, is plotted to represent them all.

In each of the graphs in Fig. 3, the straight line on the left may be taken to represent approximately readings taken over the fovea and rod-free area alone, the middle line those over the macula including the fovea, and the right-hand line those over areas including, in addition, a portion of the periphery as well.

TABLE III*
CRITICAL FREQUENCY OF FLICKER

log R	Graph 1	Graph 2	Graph 3	Graph 4 mean	log R	Graph 1	Graph 2	Graph 3	Graph 4 mean
4.134	7.89	6.15	4.88	6.31	2.311	4.69	3.77	3.14	4.02
4.503	—	4.16	4.04	4.10	2.469	4.70	3.57	2.94	4.14
4.862	6.38	4.00	3.22	4.53	2.603	5.66	4.39	4.00	4.76
3.210	4.39	2.24	2.00	2.88	2.719	5.71	4.28	3.94	4.79
3.515	4.44	3.14	2.38	4.38	2.912	6.00	4.21	5.26	5.53
3.709	3.60	3.70	2.94	4.02	1.071	6.12	5.12	4.44	5.35
3.867	4.08	3.70	3.14	4.34	1.205	8.85	4.87	5.12	6.24
2.001	4.88	3.63	3.22	4.32	1.321	12.07	6.66	5.88	7.89
2.117	4.35	3.38	3.50	3.87					

*Fig. 3.

NOTE:—R is the area of retinal illumination (square inch).

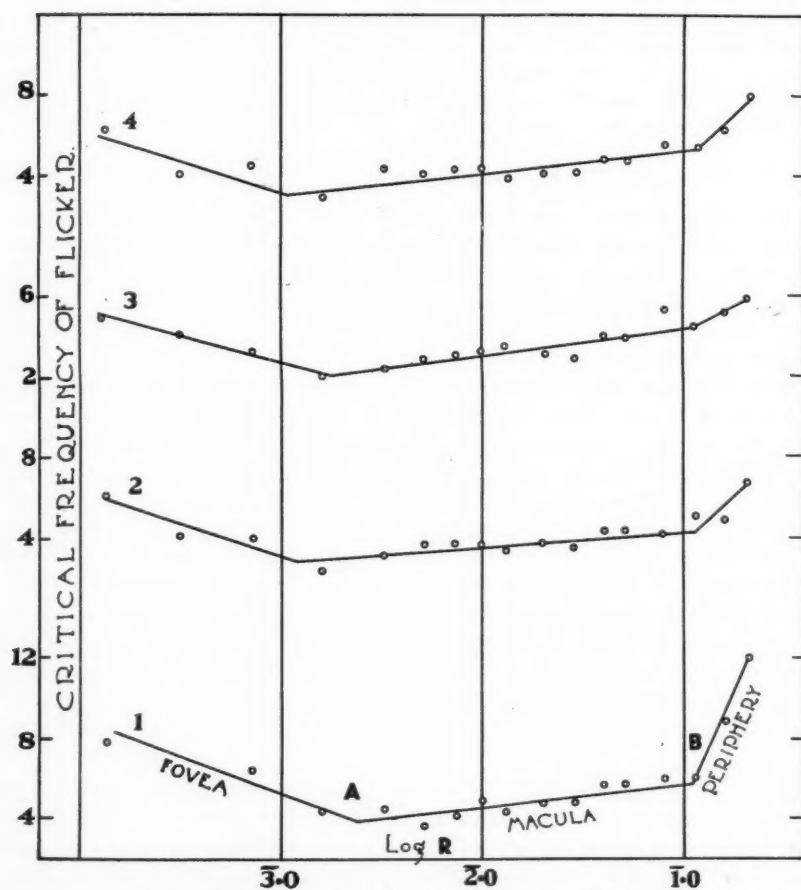


FIG. 3. A is the boundary of the fovea; B is that of the macula.

The negative slope of the line representing foveal areas indicates that as the area increases, the critical frequency of flicker required to induce the scotoscopic effect diminishes, or, its reciprocal, the duration of a flash of light on the area, increases. Presumably this fact means that by increasing the foveal area stimulated a diminution of its sensitivity results. The small positive slope of the central macular line would accordingly mean that, by increasing the stimulated area of the macula, an increase of its sensitivity is produced; and the greater positive slope of the third line indicates that, by including a portion of the periphery in the stimulated region, the sensitivity of the whole area is enhanced. These observations also demonstrate the well-established fact that retinal areas are not completely independent in their actions, but, when stimulated, mutually influence the responsiveness of each other.

The lines constituting the graph conform to the equation,

$$N = \mp k \log R + C$$

where N is the critical frequency of flicker, R is the retinal area on which the scotoscopic effect is obtained, and k and C are constants which have different values for the three lines. The minus sign represents the negative slope of the foveal line, and the plus sign the positive slopes of the other two lines.

The complete graph is now found to consist of three straight lines with two points, A and B, of intersection. Since in all the graphs these points have approximately the same positions, some special significance, which appears to be connected respectively with the areas of the fovea and macula, must attach to them.

The fovea centralis, the area of distinct vision, is a slight depression in the centre of the macula lutea or yellow spot. It contains only cones, while in addition, a small surrounding region is also free from rods. In the macula, rods become interspersed among the cones, and as the area widens they increase gradually in number until, in the outer periphery of the retina, they are found in abundance with cones sparsely scattered among them.

Since the fovea is not a sharply defined depression, it is difficult to fix its boundary exactly. The measurements of its diameter, which varies in size in different individuals, have consequently rather largely divergent values. In many treatises on physiological optics the diameter is given as 0.2 to 0.4 mm., while the area is stated to be from 0.5 to 0.6 sq. mm. Obviously the diameters mentioned will not give these areas, since for the larger value the fovea would have an area of only 0.13 sq. mm., which is much too small to serve the purpose of distinct vision. It is also noteworthy that such measurements are made on preserved preparations of the retina. In living eyes (5, p. 339) the ophthalmoscope gives foveal diameters of 0.5 to 0.75 mm. Other measurements are quoted by Parsons (7, p. 13). Koster, for example, states that the rod-free area, which includes the fovea and its immediate surroundings, varies in diameter from 0.44 mm. for a child, to 0.901 mm., for a youth 20 years old; and he mentions also individual values of 0.5 and

0.88 mm., the latter being the probable value for an adult. He also states that rods are comparatively scanty over an area even larger than that corresponding to the diameter 0.901 mm. This is the diameter of a rod-free area of 0.64 sq. mm., which is about the value mentioned above. Dimmer also, according to Parsons, described a fovea no less than 1.5 mm. in diameter. In addition to these values, Fritsch, as quoted by Howell (5, p. 339), found diameters as large as 0.75 mm. for the fovea alone when measured from the edges of the depression.

Since Graph 4 in Fig. 3 represents the mean of the three experimental graphs in the figure, the points *A* and *B* on it may be used to obtain the experimental values of the foveal or rod-free, and the macular, areas derived from the scotoscopic effect. The intersection point *A* represents a value of 0.0011 sq. in., or 0.71 sq. mm., which gives a diameter of 0.94 mm. for the rod-free area. These quantities agree fairly well with the values 0.64 sq. mm. and 0.901 mm. in the preceding paragraph.

In regard to the area of the macula there is also much discordance in the measurements. Treatises (7, p. 13) on color vision give values of 1 to 3 mm. for the diameter. According to Howell (5, p. 339), diameters of 6 mm. for this region have been found. In the macula, rods begin to appear, at first dispersed singly among the cones but gradually increasing in numbers, each cone becoming surrounded by a circle of rods. Maximow and Bloom (6, p. 584) have found that at a distance of 4 or 5 mm. from the fovea a notable increase in the relative number of rods occurs, which quickly reaches the condition where three or four rows of rods find room between two cones. This arrangement persists to the periphery of the optic part of the retina, where cones again become more numerous. In each retina the rods number 130,000,000 and the cones 7,000,000. The fovea contains only cones to the number of 4,000.

The visual significance of the macula does not lie altogether in its yellow coloration, but probably even more in the relative number of rods and cones. It is reasonable to suppose that where the cones surpass the rods in number, a condition of visual responsiveness prevails which differs from that obtaining where the rods outnumber the cones. The critical area appears to be reached when its radius is about 5 mm., or its diameter is about 10 mm. The area corresponding to this radius is about 79 sq. mm. This area no doubt extends beyond the macula or yellow spot itself.

The intersection point *B* in Graph 4, Fig. 3, represents a circular area of 0.115 sq. in., or 74 sq. mm., with a radius of about 4.9 mm., or a diameter of 9.8 mm. The agreement between the two sets of values is thus fairly close.

The comparative values of the combined foveal and parafoveal rod-free area and the similarly combined macular and paramacular area, which are obtained by observation of the scotoscopic effect and by retinal measurements,

are shown diagrammatically in Fig. 3-A. The respective radii for these areas are, for the fovea, 0.475 and 0.45 mm., and for the extended macula, 4.9 and 5 mm. In the figure the continuous circles represent the measured, and the broken circles, the scotoscopic values.

The criticism may be offered that the largest retinal measurements have in both cases been used in comparison with the scotoscopic values. The selection has been made, however, for two reasons. First, the retinal measurements have been made on preserved, stained and fixed specimens, and some shrinkage of the tissue must inevitably occur in the various processes. Second, the areas where the scotoscopic effect undergoes critical changes must in the nature of the effect be the largest possible areas, since a decided change in structure must occur before the scotoscopic effect can be so abruptly changed in its critical frequency as the graphs indicate.



FIG. 3-A. Continuous circles denote areas obtained from retinal measurements. Broken lines denote areas obtained from scotoscopic effect. Diameters are approximately to same scale, $\times 20$.

Effect of Unequal Illumination of the Tube and Screen

In this series of experiments there is shown the effect of varying the illumination of the tube, while that of the screen viewed through the hole in the disc at the end of the tube remained constant. The screen was illuminated by the light from only one lamp; while the tube was illuminated in succession by one, two, three, four and five lamps. In Table IV are given the measurements of the critical frequency of stimulation required to excite the scotoscopic effect, and they are shown graphically in Fig. 4. The graphs are marked from 1 to 5, and the same figures give the number of lamps illuminating the tube. The numbers also approximately represent the ratio of the surrounding to the central retinal illumination.

The graphs have the same threefold linear structure as before, and the points of intersection of the lines represent the same retinal areas of fovea and macula that were previously found. The greatest range of magnitudes in the observations, as the graphs show, occurred with the ratio of 2 to 1, the differences becoming less pronounced with ratios both larger and smaller than this somewhat critical value.

TABLE IV*
CRITICAL FREQUENCY OF FLICKER

log R	Ratio 1 : 1 Graph 1	Ratio 2 : 1 Graph 2	Ratio 3 : 1 Graph 3	Ratio 4 : 1 Graph 4	Ratio 5 : 1 Graph 5
4.134	5.71	6.38	4.54	2.94	4.08
4.503	4.16	3.84	2.56	2.27	2.66
4.862	3.33	2.98	2.84	2.10	2.59
3.210	2.43	1.72	2.79	1.73	1.94
3.515	2.94	2.74	2.32	2.22	1.90
3.867	3.07	2.17	2.38	2.50	2.15
2.117	2.43	2.94	2.27	2.40	2.56
2.469	2.27	2.66	2.29	2.50	2.46
2.719	2.85	2.70	2.32	2.85	2.59
2.912	2.66	4.76	2.70	2.94	2.66
1.071	3.03	3.22	3.03	3.03	2.82
1.205	2.98	3.50	3.44	3.14	2.81
1.312	3.77	3.41	3.57	3.54	2.81
1.423	3.70	4.81	3.44	3.96	3.22
1.515	4.34	6.00	4.44	4.17	3.39
1.598	4.54	5.40	4.88	4.49	3.84

*Fig. 4.

NOTE:— R is the area of retinal illumination (square inch).

The ratios are the number of lights on the tube to the number on the field.

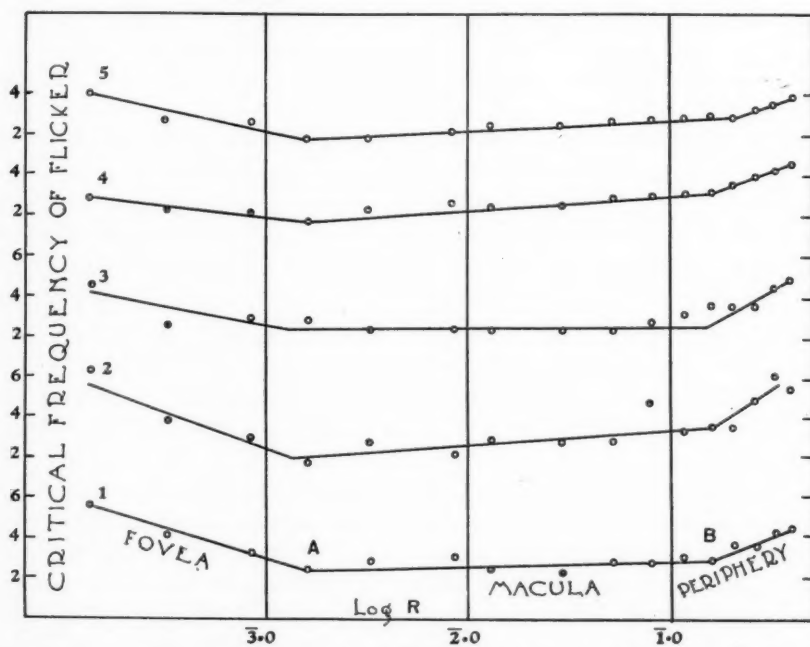


FIG. 4. A is the boundary of the fovea; B is that of the macula.

General Considerations

The effects exhibited by dark and by illuminated tubes are not two different kinds of phenomena but only different phases of the same retinal activities. When the periphery of the retina is more brightly illuminated than the centre, the former inhibits the sensitivity of the latter with the result that there is a reduction of the brightness of the central patch of light. As the illumination of the periphery is diminished, the darkening of the central patch becomes less pronounced, since there is less inhibitory action upon it. When the illumination of the whole retina is normal, or when no tube is used, no central darkening is noticeable. If vision is directed through a dark tube, the inhibitory action exerted upon the centre from the periphery is eliminated, and is replaced by facilitation which enhances the brightness of the central field. The more complete is the removal of all illumination or stimulation from the periphery, as with long and narrow tubes, the greater is the enhancement of brightness of the central area or of the response to constant stimulation.

In studying the darkening of the field with an illuminated tube, it is possible by using a rotating sector disc to obtain and measure an end-result which has been called the scotoscopic effect. No analogous end-result was found by which to measure the brightening or photoscopic effect of a dark-tube. Probably one of some kind exists, and doubtless further investigation will disclose it.

Under ophthalmoscopic examination, the living retina has generally a uniform red color, which is due to the visual purple or rhodopsin, and it exhibits little difference in appearance, except at the blind spot, from centre to periphery. On the red background the foveal depression shows as a minute bright point. Despite its name, the macula lutea does not present a yellow appearance. But in non-living specimens the yellow color becomes apparent. Probably on this account Gullstrand (4) expressed the opinion that the yellow coloration is only a post-mortem effect. Against this view are ranged some visual color phenomena which are usually explained by selective absorption in the yellow spot.

The appearance of the living retina, as well as its structure, do not seem therefore to impose precise boundaries upon the macular area. Possibly some of its characteristic visual properties are due to the change from predominantly cone structure to predominantly rod formation, with perhaps a transition in function occurring in the region where the rods and cones are equal in number. Or, since each cone has a nerve fibre attached to it, while generally two or three rods are together upon a single fibre, a transition may occur where not the number but the functions of the cones yield ascendancy to those of the rods.

Conspicuous among the visual properties of the rod-free foveal and para-foveal region is its relatively high threshold value for light and its consequent insensitivity to weak light. The foveal region is therefore subject to night-blindness. There is also an almost complete absence of dark adaptation.

Possibly in these visual characteristics of the central parts of the retina the explanation of the scotoscopic effect is to be found, and it is accordingly tentatively suggested.

The presence of bright light upon the periphery of the retina excites an inhibitory influence upon the responsiveness of the central region whereby the area of the screen viewed through the highly illuminated tube becomes darkened in appearance. When the sectorized disc is rotated in front of the tube, a further reduction in the visual intensity of the light seen through it occurs according to Talbot's law; and the combined influence of both factors may bring its visual intensity below the threshold value. The perception of light is thereby completely inhibited. This results in the scotoscopic effect.

As soon as the area upon which the scotoscopic effect is observed widens sufficiently to include rods in its structure, the critical frequency of rotation of the disc, at which the scotoscopic effect occurs, abruptly changes. This is shown by the intersection point *A* in Fig. 3.

Over the macula, rods become mingled with cones in gradually increasing numbers, until a critical area is reached where rod vision begins to predominate over cone vision. This condition is represented in Fig. 3 by the occurrence of the second intersection point *B*.

In Fig. 3 there is, first, a downward slope of the graphs corresponding to the rod-free foveal area; then, second, a gradual rise in slope for the macular area of mingled rods and cones, but predominantly cone vision; finally, there is a sharp rise in the slope of the graph corresponding to the area wherein rod vision begins to predominate.

The Scotoscopic Effect with Complementary Colors

The final part of the present investigation was to discover whether or not the scotoscopic effect could be obtained with complementary colors. For this purpose pure spectral colors would have been the proper sources of stimulation. An attempt was made to employ such spectroscopic apparatus as was available, but without success. It was therefore decided to make a preliminary investigation with colored papers.

Colored tissue papers were accordingly examined to secure if possible pairs which transmitted complementary colors. Pairs of such papers were placed in a stereoscope by which the transmitted colors could be visually fused, in order to select such as would give a white appearance. Success was obtained with hues of blue and yellow. The tube and field were then covered with the yellow paper, and the opaque sectors of the disc with the blue, which was quite dark in appearance. With this combination of colors it was found that at the critical frequency of flicker the blue color disappeared, giving place to a most intense black which at times became slightly tinged with purple. A set of discs which fitted the end of the celluloid tube was prepared with central holes of the same size as those used in the former experiments with white light.

Three sets of observations were made which are given in Table V, and are plotted in Fig. 5. The three graphs are of the same form as those obtained with white light, though not of so pronounced a character. The intersections of the lines occur at a larger foveal but the same macular area as before.

TABLE V*
CRITICAL FREQUENCY OF FLICKER

log R	Graph 1	Graph 2	Graph 3	log R	Graph 1	Graph 2	Graph 3
4.503	2.25	1.72	2.31	2.603	4.59	2.70	3.03
4.862	2.50	1.90	2.63	2.719	3.07	3.03	2.94
3.210	2.50	1.84	2.85	2.912	4.65	3.33	3.17
3.515	2.15	2.00	2.38	1.071	3.81	3.57	3.44
3.709	2.08	1.90	2.43	1.205	4.10	3.67	3.50
3.867	2.35	1.92	2.17	1.321	4.87	3.54	3.84
2.001	2.50	1.94	2.17	1.423	4.82	4.65	4.16
2.117	2.81	2.24	2.40	1.515	5.26	4.44	4.49
2.311	2.50	2.35	2.38	1.598	6.52	4.88	5.26
2.469	3.22	2.50	2.56				

*Fig. 5.

NOTE:—R is the area of retinal illumination (square inch).

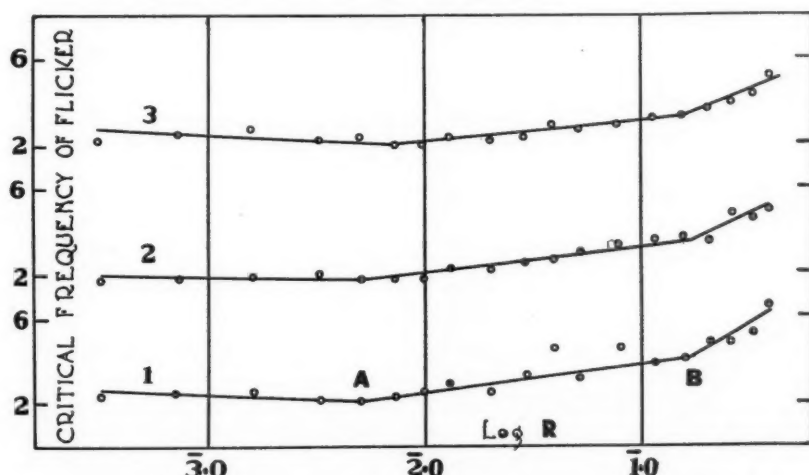


FIG. 5. A is the boundary of the fovea; B is that of the macula.

The blue and yellow colors were then interchanged and the observations renewed. A slight darkening effect was noticed, but not sufficiently pronounced to give measurable results. The intensity of illumination was varied as much as the arrangements rendered possible without, however, enabling the scotoscopic effect to be obtained.

A combination of red and green papers, which were not nearly as complementary as the blue and yellow, was then examined. A darkening effect was perceptible but not sufficiently definite to give any measurements.

Other changes in the appearance of colors, when viewed under the conditions described, were observed, but only sufficiently to show that their explanation would require more complete study than it was possible to give in the present investigation. When it is remembered that there are three color sensations, red, green and violet, all of which are susceptible of partial or complete inhibition individually or in pairs, it will be realized how complicated the color effects may possibly become.

The striking examples of inhibitory influences extending from one retinal area to another constitute additional evidence of the operation of sensory reflex actions which have formerly been described in several papers by one of the authors (1). The neural mechanism of the reflex arc required to produce the observed effects has not yet been traced. But since the effect is observed, the cause must exist, and it will no doubt ultimately be found by microscopical analysis of the nervous tracts involved.

References

1. ALLEN, F. J. *Optical Soc. Am.* 7 : 583-626. 1923.
2. ALLEN, F. J. *Optical Soc. Am.* 7 : 913-942. 1923.
3. ALLEN, F. J. *Optical Soc. Am.* 9 : 375-388. 1924.
4. GULLSTRAND, A. *Arch. Ophthal.* 62 : 1. 1905 ; 66 : 141. 1907.
5. HOWELL, W. H. *Textbook of physiology*, 8th ed. W. B. Saunders, Philadelphia.
6. MAXIMOW, A. A. and BLOOM, W. *Textbook of histology*. 2nd ed. W. B. Saunders, Philadelphia. 1930.
7. PARSONS, J. H. *Colour vision*. 2nd. ed. Cambridge Univ. Press. 1924.
8. SHERRINGTON, C. S. *Integrative action of the nervous system*. Yale Univ. Press, New Haven. 1920.
9. TSCHERNING, M. H. E. *Physiologic optics*. English translation by C. Weiland. Keystone Publishing Co., Philadelphia. 1924.

DETERMINATION OF THE NATURAL WAVE-LENGTH OF AN ANTENNA BY THE REACTANCE METHOD¹

BY GEORGE SINCLAIR²

Abstract

The values for the natural wave-length of an antenna obtained by direct measurement and by the "intercept method" were found to disagree. In the investigation of the cause of this disagreement, a reactance method was developed for measuring the natural wave-length of an antenna. The data obtained in this method can be used to obtain points on the intercept method graph for relatively small values of inserted inductance. These points do not fall on a straight line, probably owing to variations occurring in the antenna input inductance and capacity near the natural wave-length.

Introduction

In designing the tuning and coupling system for an antenna for a broadcasting transmitter, it is necessary to know the so-called "constants of the antenna." The natural wave-length and the effective input inductance and capacity of the antenna must be known in order to calculate the size of loading coil required. It is customary to determine these constants experimentally, since they cannot be readily calculated with an accuracy sufficient for engineering purposes.

In the course of the measurement of the natural wave-length of the antenna at the University of Alberta Radio Station CKUA, it was found that the results obtained by using two different methods did not agree satisfactorily. The antenna, which is of the inverted-L type, consists of a horizontal flat top 154 ft. long and a vertical up-lead 80 ft. long. Owing to the fact that the antenna is located above a sandy hill, a counterpoise system is used to reduce earth losses. The counterpoise consists of 12 wires, spaced 3 ft. apart, and insulated from the ground.

Experimental

Several methods are employed for the measurement of the natural wave-length, but direct measurement and the "intercept method" are the two most common. In investigating the cause of the difference in the results obtained by these two methods, a third method for measuring the natural wave-length was developed. Each of these will be discussed in turn.

Direct Measurement of the Natural Wave-length

Perhaps the simplest method of obtaining the natural wave-length of an antenna is to measure it directly. Consideration must be given, however, to the method used for feeding energy to the antenna. A coupling coil cannot be used because its inductance changes the resonant wave-length of the antenna. To overcome this difficulty it has been suggested (1, p. 400)

¹ Manuscript received March 10, 1936.

Contribution from the Department of Electrical Engineering, University of Alberta, Edmonton, Alberta.

² Graduate student, Department of Electrical Engineering, University of Alberta.

that an oscillator of sufficient power be employed to produce a measurable current in the antenna with no coupling other than that furnished by the antenna and up-lead. Application of this method to the antenna-counterpoise system yielded a value of 326 metres for the natural wave-length.

The Intercept Method

In the so-called "intercept method" for measuring the natural wave-length of an antenna, various sizes of accurately calibrated inductance coils are inserted in series with the up-lead of the antenna, and the resonance wave-lengths obtained. It can be shown (1, p. 398) that if the effective input inductance and capacity of the antenna are constant, then a graph drawn with wave-length squared as ordinate, and inserted inductance as abscissa, will be a straight line. This line intercepts the wave-length squared axis at a point corresponding to the natural wave-length.

In performing this experiment on the antenna-counterpoise system, care was taken to eliminate the effects of distributed capacitance in the inductance coils by calibrating each coil at the frequency at which it was used. This was done by employing a double-pole double-throw switch to connect the inductance coil and a thermomilliammeter, either to the antenna and counterpoise or to a calibrated condenser. After tuning the oscillator so as to cause the antenna circuit to resonate, the switch was changed to connect the condenser in series with the coil, the condenser being varied to resonate with the coil. Knowing the capacity of the condenser and the wave-length, a value for the effective inductance of the coil, at the wave-length used, can be readily obtained.

The graph was drawn for the antenna-counterpoise system and the line was found to be straight, showing that the antenna inductance and capacity are substantially constant over the range covered by the experiment. The intercept on the wave-length squared axis gives a value of 316 metres for the natural wave-length of the antenna.

The value for the natural wave-length, as obtained in this experiment, is about 3% less than that obtained by direct measurement. This difference seemed to be too large to be ascribed to unavoidable experimental errors. The divergence is readily explained, however, by a variation occurring in the values of the antenna inductance and capacity. It can be shown by a mathematical analysis of an antenna, that the antenna input inductance and capacity increase slightly as the natural wave-length is approached (1, p. 390). Assuming this to be true, it is apparent then that the intercept graph is inaccurate for small values of inserted inductance. It is difficult to obtain points on the graph with small values of inductance using the regular intercept method, owing to the difficulty of accurately measuring the small inductance. In order to obtain points on the graph for small values of inserted inductance, another method for measuring the natural wave-length was developed which allows these points to be easily obtained. For convenience, the new method will be designated the "reactance method", in this paper.

The Reactance Method

If a variable condenser and an inductance coil are placed in series with the up-lead of an antenna, the resonance wave-lengths can be obtained for various settings of the condenser. At any given wave-length, the combined reactance of the coil and condenser must be a reactance equal in value and opposite in phase to the input reactance of the antenna. At the natural wave-length of the antenna, the input reactance is zero. Therefore, if the entire circuit of coil, condenser, and antenna are in resonance at the natural wave-length of the antenna, the resultant reactance of the coil and condenser in series must be zero, *i.e.*, the reactance of the coil equals the reactance of the condenser, and they form a resonant circuit in themselves. Thus, if the inductance of the coil and the capacities required to tune the antenna circuit to various wave-lengths are known, curves of their reactance can be drawn with wave-length (or frequency) as abscissa. At the natural wave-length of the antenna the two curves will intersect, and thus the natural wave-length can be obtained by determining the point of intersection.

Also, the ordinate between the two reactance curves will be the reactance required to tune the antenna. For wave-lengths longer than the natural wave-length, this reactance will be inductive. Hence the value of an inductance which would have the same reactance as this resultant reactance can be calculated. If this is done for various wave-lengths, data are obtained which can be used to draw a graph similar to that obtained in the intercept method. Since the two reactance curves can be quite definitely determined in the region of the natural wave-length, values for the intercept graph can be obtained for small inserted inductances.

The circuit used is shown in Fig. 1. A double-pole double-throw switch (DPDT) was employed to eliminate the effects of distributed capacity in

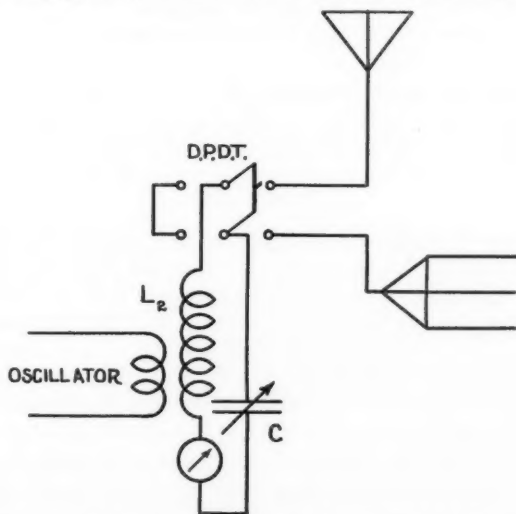


FIG. 1. Circuit for measuring the natural wave-length of an antenna.

the inductance coil, by calibrating the coil at each wave-length used, as was done in the intercept method. It was found that care must be taken in arranging the circuit, otherwise "hand-capacity" effects may be present and give erroneous results. The case of the condenser should be at a low potential with respect to ground. It is not permissible to ground any point in the antenna circuit except the so-called "neutral point". In the present case no ground connection was employed, so the apparatus was kept well away from grounded metal objects.

The reactance curves obtained are shown in Fig. 2. Frequency has been used for abscissa, instead of wave-length, since it is more convenient to use frequency in calculating reactances. The curves intersect at a frequency of

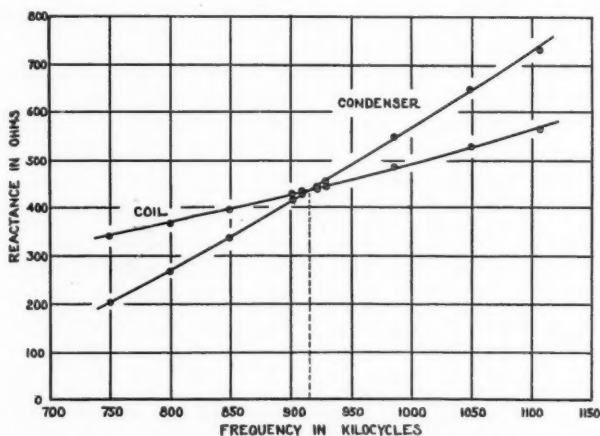


FIG. 2. Curves relating reactances of coil and condenser with frequency.

918 kc., which corresponds to a wave-length of 327 m. This value for the natural wave-length agrees with that found by direct measurement, within the accuracy of the experiments. This method gives the true natural wave-length, since it is independent of the variation in the antenna input capacity and inductance.

The value of an inductance equivalent to the combined coil and condenser, at any given frequency, can be readily calculated from the two settings of the condenser, and the frequency, as follows:

- Let f = the frequency of the oscillator,
- L_2 = the inductance of the coil,
- C_1 = the capacity required to tune the antenna and coil to the frequency f ,
- C_2 = the capacity required to tune the coil alone to the frequency f ,
- L = the inductance equivalent to the coil and condenser in series, at the frequency f .

Then,

$$\begin{aligned}
 2\pi fL &= 2\pi fL_2 - \frac{1}{2\pi fC_1} \\
 2\pi fL &= \frac{1}{2\pi fC_2} - \frac{1}{2\pi fC_1} \\
 &= \frac{1}{2\pi f} \left(\frac{C_1 - C_2}{C_1 C_2} \right) \\
 \therefore L &= \left(\frac{1}{2\pi f} \right)^2 \left(\frac{C_1 - C_2}{C_1 C_2} \right) \quad (1)
 \end{aligned}$$

Values for the inductance L can thus be readily calculated and a graph drawn with wave-length squared as ordinate and inductance L as abscissa. The graph obtained is shown in Fig. 3 (Curve 1). The wave-length is in

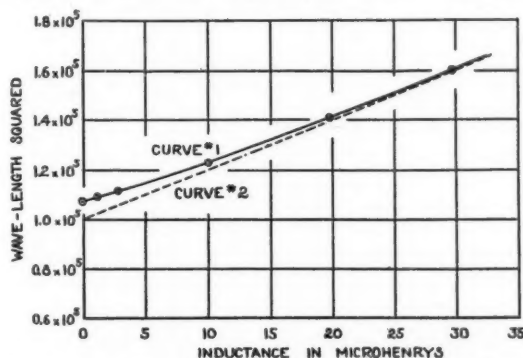


FIG. 3. Graphs for the "intercept method" for small values of added inductance.

metres. A portion of the straight line obtained in the intercept method has also been drawn for purposes of comparison (Curve 2). It can be seen that the two graphs lie together at long wave-lengths, but diverge as the natural wave-length is approached. This divergence means that the antenna input inductance and capacity vary near the natural wave-length. The reactance method thus gives an interesting proof of the variation that occurs in the "constants" of an antenna.

Conclusions

As a result of this variation in the "constants" of an antenna, it is necessary to decide which value of the natural wave-length should be used in design problems. Since, for wave-lengths appreciably longer than the natural wave-length the antenna behaves as though its input inductance and capacity are constant, values for the constants obtained from the regular "intercept" graph should be used. Any variation in the antenna "constants" that occurs near the natural wave-length does not affect calculations made for longer wave-lengths. As the natural wave-length is approached, however, the effective input inductance and capacity vary, causing the apparent natural wave-length to change, and the usual intercept graph cannot be used for purposes of design.

Acknowledgments

The author wishes to express his sincere thanks to Dr. H. J. MacLeod, for supervising these experiments, and to Mr. D. G. Williams, for his assistance in performing the experiments.

Reference

1. MOULLIN, E. B. Radio frequency measurements. Charles Griffin and Co., London. 1931.

Canadian Journal of Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOL. 14, SEC. B.

APRIL, 1936

NUMBER 4

STUDIES ON LIGNIN AND RELATED COMPOUNDS

XXII. FRACTIONATION OF METHANOL LIGNIN¹

BY JACK COMPTON², MARGARET GREIG³ AND HAROLD HIBBERT⁴

Abstract

Preparation of methanol lignin by the method of Brauns and Hibbert on a larger scale than that employed previously has disclosed the presence of a second fraction, soluble in ether-dioxane. The original methanol lignin and this new fraction are obtained in a pure state by fractionation with dioxane and benzene. The former has been shown to correspond to the methanol lignin from which the Brauns and Hibbert formula $C_{42}H_{32}O_6(OCH_3)_6(OH)_4$ was derived. The benzene-dioxane-soluble fraction has been methylated and acetylated, and shown to have a different composition, the ratio of methoxyl to hydroxyl groups being 5 : 3.

Introduction

Brauns and Hibbert (1) prepared methanol lignin on a small scale by heating spruce wood meal in a sealed tube with a 2% solution of anhydrous hydrogen chloride in absolute methanol at 90° C. for four days, agitation being accomplished by mechanically tilting the tube. The crude methanol lignin, representing about 25% of the total lignin of the wood, was purified by solution in dioxane and precipitation in ether. The methoxyl content of the purified material was 21.6%. On methylation with diazomethane this increased to 24.9%, and, on complete methylation, to 32.4%. From these results they calculated for the original lignin an empirical formula $C_{48}H_{54}O_{16}$ (indicating a molecular weight of 886) or, expanded, $C_{42}H_{32}O_6(OCH_3)_6(OH)_4$. Only one lignin fraction, insoluble in ether-dioxane, was isolated, the yield of this being about 80% of the crude methanol lignin.

On repeating the preparation on a larger scale, the presence of a second fraction, soluble in ether-dioxane and in benzene-dioxane, was disclosed. This material has a methoxyl content of 23.9% and amounts to rather less than 20% of the crude methanol lignin. This is in accordance with the results of Brauns and Hibbert.

It was found in the present investigation that purification of the ether-insoluble methanol lignin was more difficult of accomplishment than in the earlier work (1), since on repeated precipitation from dioxane into ether the

¹ Manuscript received March 10, 1936.

Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, Montreal, Canada, with financial assistance from the Canadian Pulp and Paper Association and Canadian International Paper Company.

² Research Chemist, Division of Industrial and Cellulose Chemistry, McGill University.

³ Holder of Canadian International Paper Company Research Scholarship.

⁴ Professor of Industrial and Cellulose Chemistry, McGill University.

methoxyl remained constant at 22.2%, a higher value than that found by Brauns and Hibbert (OCH_3 , 21.6%). However on repeated precipitation from dioxane into benzene, in which the true benzene-insoluble methanol lignin is insoluble, this latter was obtained with a methoxyl content of 21.0%, exactly that calculated on the basis of the Brauns-Hibbert lignin formula (1). The ether-dioxane-soluble fraction was precipitated with petroleum ether both from ether-dioxane and benzene-dioxane solutions with a constant methoxyl content of 23.9%. The ratio of insoluble (OCH_3 , 21.0%) to soluble fractions (OCH_3 , 23.9%) was about 4 : 1 when the extraction was carried out at 70–75° C. At 90–100° C. the proportion of ether-insoluble was much less, approximately 2 : 1.

The identity of the ether-insoluble methanol lignin (OCH_3 , 21.0%) with that obtained by Brauns and Hibbert is shown by the results recorded in Table I.

TABLE I

	Found in present work		Found by Brauns and Hibbert	Calcd.	
	OCH_3 %	S %	OCH_3 %	OCH_3 %	S %
1. Ether-insoluble methanol lignin	21.0	—	21.6	21.0	—
2. Same, acetylated	17.4	—	17.8	17.6	—
3. Same, diazomethane-methylated	24.7	—	24.6	24.1	—
4. Toluene sulphonic ester of No. 3	16.2	7.2	Not prepared	15.9	7.0

Acetylation and methylation of the ether-soluble fraction (OCH_3 , 23.9%) show the presence of free hydroxyl groups. The methoxyl values found after acetylation and methylation are 20.2% and 34.8%* respectively, which indicates a ratio of (OCH_3) : (OH) of 5 : 3. The values calculated on this basis are 20.0 and 36.0% respectively. It follows that the ether-soluble fraction of methanol lignin differs in composition from the ether-insoluble.

Fractionation of a methanol lignin (prepared by prolonged extraction at a low temperature) by means of dioxane and ether, gave two products, one ether-insoluble, OCH_3 22.2%, the other ether-soluble, OCH_3 24.2%. The latter is clearly identical with the benzene-soluble fraction isolated above. The former has the same methoxyl value as the original ether-insoluble fraction from the lignin prepared at 90–100° C., and appears to represent a similar mixture of ether-soluble and ether-insoluble fractions. The yield of the ether-soluble fraction apparently decreases as the temperature of extraction is lowered.

*Probably not completely methylated. OCH_3 , 1st methylation 32.6; 2nd methylation 34.8%. No further methylations were carried out.

Experimental

Preparation of Methanol Lignin

Spruce wood meal (375 gm.), previously dried under reduced pressure at 50° C., was placed in a pressure autoclave, lined with glass-enamel, and three litres of a 2% solution of anhydrous hydrogen chloride in methanol was added. The mixture was stirred continuously and the temperature maintained at 90–100° C. (pressure 55–60 lb.) for approximately three days. The reaction mixture was filtered through a Büchner filter and the residual wood meal washed with methyl alcohol. Weight of wood meal residue (air-dried), 333 gm. The alcoholic solution was evaporated under reduced pressure at 40° C. During the process of concentrating this solution to about 200 cc., a crystalline material (11 gm.) separated. This was shown from its melting point, the preparation of its phenyl hydrazone, and its rotation to be α -methyl-*d*-mannoside. (M.p., 191–192° C.; $[\alpha]_D$, 80.8; OCH₃, 15.4%; phenyl hydrazone, m.p. 189° C. with decomposition.) The α -methyl-*d*-mannoside was removed by filtration and the crude lignin precipitated by pouring the methyl alcohol solution, with stirring, into distilled water. The product was then filtered and washed with water. Yield of lignin, 26.4 gm., or 25% of theoretical. OCH₃, 22.5%.

Fractionation of the Crude Methanol Lignin

The crude methanol lignin was dissolved in 260 cc. of dioxane and the solution added in a fine stream, with stirring, to 10 volumes of anhydrous ether. Yield of ether-insoluble lignin, 17 gm.; OCH₃, 22.4%. On reprecipitation in the same manner the yield was 13 gm.; OCH₃, 22.2%.

Ether-dioxane-insoluble lignin (8 gm., OCH₃, 22.2%) was dissolved in 80 cc. of dioxane and reprecipitated by pouring it dropwise, with stirring, into 800 cc. of anhydrous benzene. The mixture was filtered and washed with benzene and petroleum ether. Yield, 7 gm.; OCH₃, 21.8%. This product (7 gm.) was reprecipitated in the same manner. Yield, 7.2 gm.; OCH₃, 21.1%: after a third similar precipitation, OCH₃, 21.0%.

Isolation of the Ether-dioxane-soluble Lignin Fraction

The ether-dioxane solutions from the previous precipitations were combined and evaporated until the volume was approximately 100 cc.; the solution was then filtered and added dropwise to petroleum ether. Yield, 13.3 gm.; OCH₃, 22.9%.

A portion (8 gm.) of this product was dissolved in a mixture of 70 cc. of benzene and 10 cc. of dioxane, the solution filtered and added dropwise, with stirring, to 10 volumes (800 cc.) of petroleum ether (80–90° C.). The resulting solution was filtered and the product washed with low-boiling petroleum ether. OCH₃, 23.4%. A portion (1 gm.) of this product was dissolved in a mixture of 9 cc. of benzene and 1 cc. of dioxane and precipitated with petroleum ether (100 cc.). OCH₃, 23.8%. After the fourth precipitation; OCH₃, 23.9%.

Fractionation of Methanol Lignin Prepared at a Lower Temperature

Dry spruce wood meal (765 gm.) was exhaustively extracted with absolute methyl alcohol and hydrogen chloride at 70–75° C. for five days in the manner described in Part XX (2). The total yield of methanol lignin was 69.5 gm. OCH₃, 22.5%.

The crude material (55 gm.) was dissolved in 675 cc. of dioxane, filtered and poured in a fine stream, with stirring, into three litres of anhydrous ether, the precipitate being washed with ether and petroleum ether. Yield, ether-insoluble fraction, 44.5 gm. (= 81% of crude); OCH₃, 22.9%. The ether-dioxane-soluble portion was isolated by pouring the ether-dioxane solution, after concentration, into petroleum ether. Yield, 7.5 gm. (= 14% of crude); OCH₃, 24.1%.

The ether-insoluble fraction (1st precipitation, 20 gm.; OCH₃, 22.9%) was refractionated in the same way. Ether-insoluble: yield, 17.8 gm.; OCH₃, 22.2%. Ether-soluble; yield, 1.05 gm.; OCH₃, 24.5%. A third fractionation of the ether-insoluble portion (17.8 gm.) gave 17.0 gm. of ether-insoluble (OCH₃, 22.3%) and 0.5 gm. of ether-soluble (OCH₃, 24.2%).

The methoxyl value of the ether-soluble fraction agrees with that found above after fractionation with benzene-dioxane (23.9%). The value for the ether-insoluble is identical with that obtained on fractionation, with ether-dioxane, of the crude methanol lignin prepared by heating at 90–100° C. for a shorter period (three days).

Acetylation of the Ether-insoluble Fraction of Methanol Lignin

Ether-insoluble methanol lignin (1.0 gm.; OCH₃, 21.3%) was acetylated with 10 cc. of pyridine and 6 cc. of acetic anhydride, and the product isolated as previously described (1). Yield: "ether-insoluble lignin" acetate, 0.9 gm.; OCH₃, 17.4%. "Ether-soluble lignin" acetate: yield, 0.2 gm.; OCH₃, 17.9%.

Methylation of Ether-dioxane-insoluble Methanol Lignin with Diazomethane

Methanol lignin (9.6 gm., OCH₃, 21.0%) was dissolved in 100 cc. of dioxane and treated several times at 10° C. with diazomethane. After the third methylation a sample (1 cc.) was removed and treated for analysis by diluting it with dioxane and heating the solution on the water bath for half an hour in order to coagulate the polymerized diazomethane. It was then filtered, concentrated, and the lignin precipitated with ether. OCH₃, 22.1%. After the fourth methylation: OCH₃, 23.3%; after the fifth methylation, 23.8%. After purifying by solution in dioxane and reprecipitation with ether: yield, 7.4 gm.; OCH₃, 24.3%. After a second purification by the same method: OCH₃, 24.7%.

*Preparation of the p-Toluene Sulphonate of Diazomethane-methylated**Methanol Lignin*

Diazomethane-methylated lignin (2 gm., OCH₃, 24.7%) was dissolved in 25 cc. of pyridine, and after cooling to 0° C. *p*-toluene sulphonyl chloride (4 gm., recrystallized) was added. The mixture stood at room temperature

for 24 hr. It was then poured into well-stirred ice water, allowed to stand for a further two hours, filtered, and washed with water. Yield, 2.9 gm.; OCH_3 , 16.2%. The crude ester (2.9 gm.) was dissolved in 29 cc. of dioxane and precipitated with anhydrous ether. Found: OCH_3 , 16.2; S, 7.2%. Calcd. from the Brauns-Hibbert formula, $(\text{OCH}_3)_7\text{C}_{42}\text{H}_{32}\text{O}_6(\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3)_3$: OCH_3 , 15.9; S, 7.0%.

Acetylation of the Ether-soluble Fraction of Methanol Lignin

Ether-soluble methanol lignin (0.5 gm.; OCH_3 , 24.2%) was acetylated as described above. After 48 hr. the acetylated product was found to be completely soluble in ether, so that, to precipitate it, it was necessary to pour the dioxane solution into low-boiling petroleum ether. Yield, 0.48 gm. OCH_3 , 20.2%.

Methylation of the Ether-soluble Fraction (Table I) of Methanol Lignin
(OCH_3 , 24.5%)

The following methylation was carried out at a temperature of 20° C., using 5% excess of 7.5 N sodium hydroxide solution. One gram of the ether-soluble fraction was dissolved in 13 cc. of acetone and then, with rapid stirring, five separate portions each of 2.65 cc. of dimethyl sulphate and of 3.9 cc. of 7.5 N sodium hydroxide solution were added simultaneously at one hour intervals. The methylated product was purified as described in detail above, except that petroleum ether (30–50° C.) was substituted for ether as precipitating agent, owing to the ready solubility of the methylated product in the latter. Yield, 0.9 gm.; OCH_3 , 32.6%.

This material was remethylated under the same conditions. Yield, 0.8 gm.; OCH_3 , 34.8%.

References

1. BRAUNS, F. and HIBBERT, H. Can. J. Research, B, 13 : 28-34. 1935.
2. KING, E. G. and HIBBERT, H. Can. J. Research, B, 14 : 12-19. 1936.

THE SOLUBILITY OF CARBON DIOXIDE IN AQUEOUS SOLUTIONS CONTAINING ALCOHOLS AND SUGARS¹

BY H. A. SHOWALTER² AND J. B. FERGUSON³

Abstract

A new type of solubility apparatus is described. The results of the solubility determinations of carbon dioxide at 15° C. are given for the following systems: alcohol-water, dextrose-water, levulose-water, sucrose-water, dextrose-alcohol-water and sucrose-alcohol-water. Certain incidental measurements of specific gravity and of vapor tension are also given.

Introduction

Since 1850, measurements have been made by various workers on the solubilities of such gases as carbon dioxide, sulphur dioxide, methane, etc., in water, in organic liquids, in salt solutions and in suspensions of solids in water, using apparatus essentially of the Geffcken type (6, p. 259). Such methods have been criticized by Manchot (11) and by Cady, Elsey and Berger (3). In order to overcome the difficulties inherent in these procedures, Morgan and Maass (12) used a magnetic stirrer within the absorption pipette, and Hainsworth and Titus (7) repeatedly bubbled the gas through the liquid. The apparatus of the latter was later modified by Morgan and Pyne (13). One of the objectionable features of the original methods was the so-called hammering effect, the shaking of the liquid increasing the pressure on the gas bubbles. It was therefore not certain that the pressure read on the manometer was the pressure under which the gas went into solution, or that it was an equilibrium pressure.

Sugar solutions have been little used in studies of gas solubility, the only published data being those of Usher (17) on dextrose-water and sucrose-water at 20° C., and those of Findlay and Shen (4) on sucrose-water at 25° C. The only published work on systems of miscible liquids appears to be that of Müller (14), who determined the solubility of carbon dioxide in alcohol-water solutions. Probably for want of a thermostat, his temperatures varied from 14.6 to 20.3° C., and the value of his data is correspondingly reduced. In 1932, French (5) obtained a series of values for this same system, using an absorption pipette which could be detached from the manometer system and shaken. His results also are presented in this paper.

Materials

Experimental

Distilled water; carbon dioxide prepared from sodium bicarbonate; a pure, 95% alcohol; granulated cane sugar; dextrose, m.p. 145–147° C., specific rotation (α_D^{22}) = +50.0°, and which contained a trace of dextrin and less

¹ Manuscript received February 7, 1936.

² Contribution from the Department of Chemistry, University of Toronto, Toronto, Canada.

³ Graduate student and holder of a bursary under the National Research Council of Canada.

³ Associate Professor of Chemistry, University of Toronto.

than 1% of keto-sugars by Selmanoff's test; Kahlbaum's levulose, (α_D^{22}) = -91° , which was decolorized with bone black; and Kahlbaum's levulose "Aus Inulin", (α_D^{22}) = -90.1° .

Apparatus and Procedure

The initial solutions, with the exception of certain sugar solutions, were freed of dissolved air either by boiling under a reflux condenser (French) or by the repeated evacuation and shaking of the containing flask (Showalter). The last trace of carbon dioxide was removed by the former method only when air, freed of this gas, was repeatedly admitted to the heated flask. The essential details of the apparatus used to prepare certain sugar solutions are given in Fig. 1. The sugar was placed in *E* and the alcohol-water solution

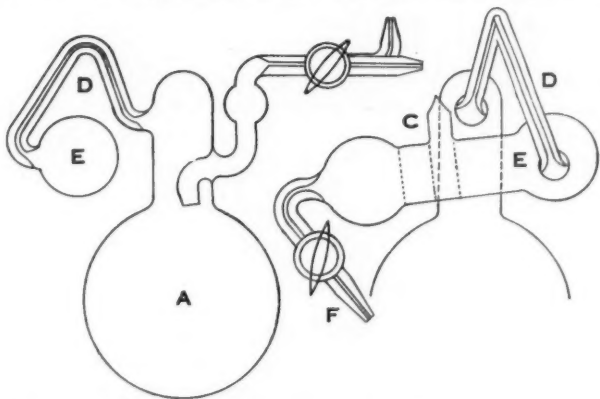


FIG. 1. Apparatus for the preparation of gas-free sugar solutions.

in *A*. The apparatus was closed, evacuated and then tilted so that a portion of the liquid flowed from *A* to *E*. After a sample, prepared in this manner, had been removed from *E*, the residual solution was diluted with fresh solution from *A*. In this way, three gas-free solutions, having different sugar contents but very nearly the same alcohol-water ratios, were prepared. This apparatus proved to be satisfactory in the case of sucrose but not so satisfactory with dextrose, which evidently contained occluded gas which was not readily removed by pumping.

The solubility apparatus is indicated, in part, in Fig. 2. The important features of it are the inverted-Y shaped absorption pipette and the stop-cock *H* which permitted this pipette to be oscillated so that the liquid flowed quietly from one leg of the Y to the other, and which enabled one to detach the pipette. The gas-free liquid was introduced into the evacuated pipette and the amount determined from the initial and final weights. This pipette was then attached to the manometer system, which was subsequently evacuated. The vapor tension of the liquid was determined. Successive amounts of carbon dioxide were introduced into the system,

measured and admitted to the absorption pipette. In this manner it was possible to determine the gas absorption by a single liquid sample at several pressures. The partial pressures of carbon dioxide ranged from 157.4 to 892.6 mm. of mercury, and a typical series, 250.5, 500.9 and 777.8 mm., indicates the kind of pressure intervals employed and the nature of the deter-

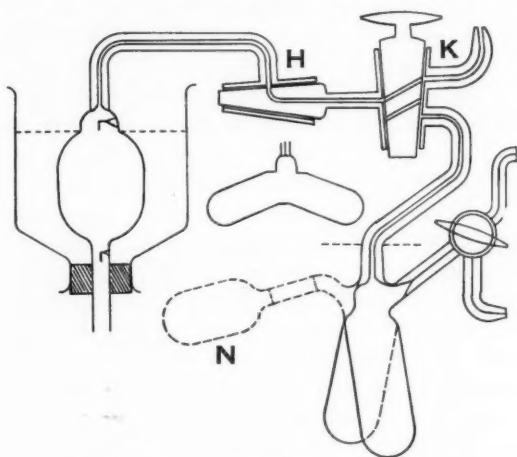


FIG. 2. Gas-measuring and absorption pipettes.

minations which are later reported for individual samples. At the conclusion of a series, the liquid was removed from the pipette, its density determined at 15° C. and at the temperature for which tabulated data were available when this method of analysis was employed. In the case of the alcoholic sugar solutions, the final liquids were separated into two fractions by distillation, the one containing the sugar, the other the alcohol; and the densities of these fractions, suitably diluted or concentrated, were determined. For the actual analyses, the tabulated densities for alcohol-water (9), for sucrose-water (8) and for levulose-water (15) were employed; for dextrose-water the values given in Table I were used.

TABLE I
THE DENSITY OF AQUEOUS DEXTROSE SOLUTIONS AT 25° C.

Wt. per cent anhyd. dextrose	4.96	8.25	14.79	18.57	25.07
D_4^{25}	1.016	1.029	1.056	1.072	1.101

From the various measurements, the necessary quantities for the calculation of the Bunsen coefficient α_{15} were readily obtained. For these calculations, carbon dioxide was assumed to obey the simple gas laws—an assumption supported by Beattie's (1) equation of state.

The temperature of the room and the small water bath was 20–25° C., that of the large thermostat containing the absorption pipette, 15° C., so that there was no tendency for vapor to condense in the external leads and gas-measuring pipette.

The volume change of the liquid after solution of the gas was found to be negligible even for solutions having values of α_{15} as high as 2.5. For these measurements, a calibrated side tube *N* was sealed to the absorption pipette.

When the whole system was evacuated and the pipette oscillated, the pressure rose less than 0.2 mm. in one hour, showing that stopcock *H* was a satisfactory seal.

The attainment of equilibrium, which required half an hour, was checked in one case in the following manner. After a constant pressure reading was obtained at 15° C., the temperature was lowered to 12.5° C., and the new constant pressure was found to be lower and the lowering greater than that which could be attributed to the lowering of the vapor tension of the liquid alone. The temperature was raised to 15° C. and the constant pressure, again noted, was identical with the initial pressure at this temperature.

Since there was no method of checking the point, the vapor tension of a liquid sample was assumed to be the partial pressure of the vapor of the liquid in the final gas phase.

Results and Discussion

The densities of aqueous dextrose solutions at 25° C. are given in Table I. These are in essential agreement with those given by Pulvermacher (16), but are more concordant. The results for the alcohol-water system at 15° C. are given in Table II and indicated in Fig. 3. The results of French, recalculated on the basis of his vapor tension measurements by Showalter, Bohr's (2) value for water and Just's (10) value for 97% alcohol are also included.

TABLE II

THE SOLUBILITY OF CARBON DIOXIDE IN ALCOHOL-WATER SOLUTIONS AT 15° C.

Weight per cent alcohol	Vapor pressure of pure solution, mm. Hg.	α_{15} (average)	Maximum deviation	No. of experiments
0	12.7	1.022	± 0.002	2
7.7	15.5	0.9910	± 0.004	3
12.2	17.5	0.9545	± 0.001	2
24.0	21.5	0.8427	± 0.001	2
34.5	25.0	0.8550	± 0.0001	3
52.6	29.0	1.130	± 0.002	2
90.8	31.2	2.546	± 0.003	3
91.8	31.8	2.556	± 0.005	2

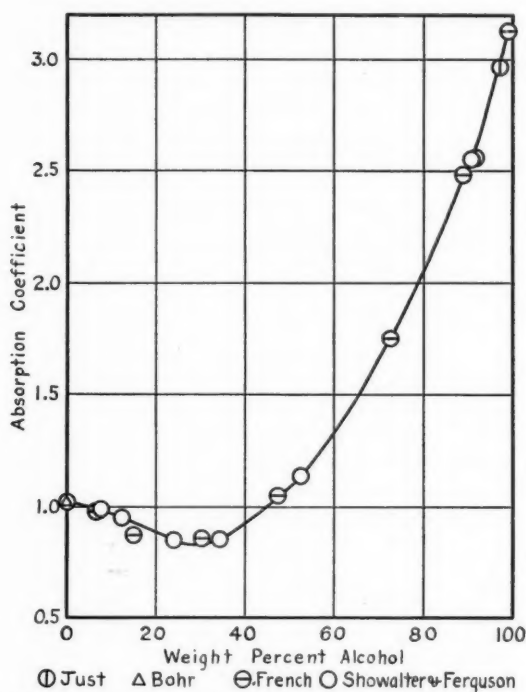


FIG. 3. The solubility of carbon dioxide in aqueous solutions of alcohol at 15° C.

The values for Kahlbaum's levulose, Table III, are the average of the values for the two higher pressures. The initial value of α_{15} for the lowest pressure differed from the other two by as much as 1% in some cases. This difference

TABLE III

THE SOLUBILITY OF CARBON DIOXIDE IN AQUEOUS SUGAR SOLUTIONS AT 15° C.

Weight per cent sugar	α_{15} (average)	Maximum deviation	No. of experiments	Weight per cent sugar	α_{15} (average)	Maximum deviation	No. of experiments
<i>Dextrose</i>				<i>Kahlbaum's levulose</i>			
4.5	0.9714	± 0.0009	2	10.7	0.9061	± 0.0032	2
9.25	0.9284	± 0.0016	3	13.6	0.8670	± 0.0020	2
11.2	0.8986	± 0.0011	3	14.1	0.8676	± 0.0012	2
15.0	0.8526	± 0.0013	3	21.2	0.7866	± 0.0010	2
21.9	0.7772	± 0.0027	3	<i>Kahlbaum's "Aus Inulin" levulose</i>			
22.4	0.7636	± 0.0031	3	6.2	0.9529	± 0.0032	3
26.9	0.7157	± 0.0014	3	12.0	0.8768	± 0.0026	3
27.9	0.7050	± 0.0010	3	23.1	0.7452	± 0.0014	3
<i>Sucrose</i>							
8.4	0.9545	± 0.0006	3				
15.7	0.8952	± 0.0019	3				
25.5	0.8026	± 0.0039	3				

was evidently due to an unknown impurity, since the levulose "Aus Inulin" gave more concordant results. The values for dextrose-alcohol-water, Table IV, at the initial alcohol percentage of 11.2 were more concordant than

TABLE IV

THE SOLUBILITY OF CARBON DIOXIDE IN DEXTROSE-ALCOHOL-WATER SOLUTIONS AT 15° C.

Weight per cent alcohol, original liquid	Weight per cent dextrose, final liquid	α_{15} (average)	Maximum deviation	No. of determinations
8.14	5.8	0.9225	± 0.0018	2
	11.7	0.8578	± 0.0002	2
	18.15	0.8061	± 0.0028	2
11.12	19.85	0.7590	± 0.0020	3

those obtained when the percentage was 8.14. The discrepancies in the latter were attributed to the method of preparation in the special apparatus, since the agreement was good for the former case in which the solution was de-gassed by evacuation after the solution of the sugar. The more erratic results for the 8.14% alcohol sample are not reported in the table. On the other hand, for the same liquid sample the results for sucrose-alcohol-water showed agreements among the values for α_{15} similar to those indicated in Tables II and III, and hence interpolated values for definite percentages of sucrose are listed in Table V.

TABLE V

THE SOLUBILITY OF CARBON DIOXIDE IN SOLUTIONS OF SUCROSE-ALCOHOL-WATER AT 15° C.

Weight per cent alcohol, initial solution	Weight per cent sucrose, final solution				
	0	5	10	15	20
	Values of α_{15}				
0	1.021	0.983	0.941	0.898	0.853
17.7	0.902	0.871	0.837	0.801	0.764
28.8	0.830	0.806	0.782	0.757	0.730
40.5	0.920	0.896	0.873	0.848	0.822
53.0	1.151	1.132	1.110	1.085	1.055

The values of α_{15} for aqueous sugar solutions are very nearly linear functions of the sugar content. In the case of sucrose-alcohol-water, they are similar functions of the sugar content for a constant alcohol-water ratio, but the effect of the sugar becomes less as this ratio increases in value.

The minimum in the curve, Fig. 3, also extends into the system sucrose-alcohol-water, as an inspection of Table V will disclose. The presence of this minimum in the solubility curve is not confined merely to the systems here discussed, but occurs in many other curves for systems containing alcohol-water. This point is being further studied.

The agreement among the two or three values of α_{15} obtained for the individual samples at widely different partial pressures of carbon dioxide would indicate that, in the pressure ranges considered, Henry's law is closely obeyed. The deviations in the more favorable cases are about 0.1% in the value of α_{15} , and it would seem probable that to some extent even these must be due to experimental errors. In many papers, details are lacking, and the only results which may be cited for comparison are those of Morgan and Maass (12) for the solubility of carbon dioxide in water. The results showed that within their experimental error the law was obeyed.

References

1. BEATTIE, J. A. *Proc. Nat. Acad. Sci.* 16 : 14-19. 1930.
2. BOHR, C. *Ann. physik.* 68 : 500-525. 1899.
3. CADY, H. P., ELSEY, H. M. and BERGER, E. V. *J. Am. Chem. Soc.* 44 : 1456-1461. 1922.
4. FINDLAY, A. and SHEN, B. *J. Chem. Soc.* 101 : 1459-1468. 1912.
5. FRENCH, R. C. Unpublished data. 1932.
6. GEFFCKEN, G. *Z. physik. Chem.* 49 : 257-302. 1904.
7. HAINSWORTH, W. R. and TITUS, E. Y. *J. Am. Chem. Soc.* 43 : 1-11. 1921.
8. INTERNATIONAL CRITICAL TABLES. McGraw-Hill Book Company, New York. 2 : 343. 1927.
9. INTERNATIONAL CRITICAL TABLES. McGraw-Hill Book Company, New York. 3 : 116. 1928.
10. JUST, G. *Z. physik. Chem.* 37 : 342-367. 1901.
11. MANCHOT, W. *Z. anorg. allgem. Chem.* 141 : 38-44. 1924.
12. MORGAN, O. M. and MAASS, O. *Can. J. Research*, 5 : 162-199. 1931.
13. MORGAN, J. L. R. and PYNE, H. R. *J. Phys. Chem.* 34 : 1578-1582. 1930.
14. MÜLLER, O. *Ann. Physik*, 37 : 24-43. 1889.
15. OST, H. *Ber.* 24 : 1636-1645. 1891.
16. PULVERMACHER, O. *Z. anorg. allgem. Chem.* 113 : 141-148. 1920.
17. USHER, F. L. *J. Chem. Soc.* 97 : 66-78. 1910.

STUDIES OF CARBON BLACK

II. THE CHANNEL PROCESS—PRODUCTION FROM THE NATURAL GAS OF TURNER VALLEY, ALBERTA¹

By L. M. PIDGEON²

Abstract

The production of carbon black in an experimental plant of the channel type is described. Carbon black has been produced from Turner Valley dry gas in yields as high as 1.3 lb. per 1000 cu. ft. The rubber reinforcing properties, methylene blue sorption, and per cent extractable are similar to those of the commercial carbon blacks available at present. The presence of hydrogen sulphide in the gas has been examined, but little effect on yields and properties was noticed with concentrations as high as 1% by volume.

Introduction

Carbon black or gas black is produced by the impingement of a luminous flame on a moving metal surface upon which the carbon is deposited. While this method produces a carbon unequalled in color and in reinforcing power in rubber, it is excessively wasteful, seldom resulting in the recovery of more than 3% of the carbon present in the hydrocarbon gas which forms the source of supply. The industry is thus able to flourish only where there are available large amounts of cheap gas which cannot be put to more profitable uses. This situation is encountered in any gas field that is remote from populated areas offering a domestic market.

Such a field exists in the Turner Valley, Alberta, where the production of gas from the naphtha separators is in excess of local domestic requirements by a factor of at least ten. No information was available as to the suitability of this gas for the production of carbon black. It was known that appreciable amounts of sulphur were present. This is a condition regarded with disfavor by producers of carbon black because of the corrosion problems which it involves; but no quantitative information could be obtained regarding the possible effect of sulphur in the gas on the properties of the carbon itself, although a number of unfavorable opinions were obtained.

This paper describes experiments carried out in a laboratory plant of the channel type in which carbon black has been produced from Turner Valley dry natural gas. The effect of the presence of hydrogen sulphide has been investigated, and the properties of the resultant carbon black examined in the light of its possible utilization as a rubber reinforcing filler.

The Channel Process

Methods of production depending upon the impingement of a luminous flame on a relatively cool surface have been classified according to the shape and arrangement of this surface. A number of types involving the use of plates and discs have been employed at various periods in the history of the

¹ Manuscript received February 21, 1936.

Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada.

² Chemist, National Research Laboratories, Ottawa.

industry. In the production of rubber blacks, however, these forms have been almost completely superseded by the channel process, although a small amount of black finding its way into the pigment industry is obtained by deposition on rollers.

In the channel process the depositing surface is the wide face of a section of channel steel which is given a reciprocating motion over a row of flames. The deposited carbon is removed by stationary scrapers that are pressed against the moving surface. A convenient number of these members are housed in a suitable building which is equipped with adjustable openings for the admission of air to the flames and the escape of waste gases. In the present investigation the essential features of this process have been duplicated as far as possible on a laboratory scale.

While the experimental technique associated with the production of carbon black by impingement methods is of the simplest nature, very little published information regarding the factors that govern the recovery and properties is available. Many of the essential factors that control the size, shape, and luminosity of the flame are almost impossible to specify in general terms, hence such published results as are available tend to apply only to the apparatus in which they were obtained.

In spite of these difficulties some progress has been made in the evaluation of the more important factors of production. Using a small experimental plant, Wiegand (9) has shown that the recovery of carbon depends primarily on the position of the depositing surface, a sharp maximum appearing for any flame. A similar conclusion was reached by Chamberlin and Rosé (1). More recently Drogin (3) published curves relating the channel height and carbon recovery in a number of specific cases.

While the number of additional variables that might conceivably influence the production of carbon black is almost infinite, there are indications that relatively few are of major importance. Chamberlin and Rose (1) found that the yield was independent of the temperature and motion of the plate, the material of the plate, the barometric pressure and moisture content of the gas. Drogin (3) has listed a number of factors that are of importance in the control of operations in a full-scale plant. Many of these variables however, such as the cleanliness of tips, feed pipes, and collectors, do not enter into the present discussion, as they are directly under the control of the operator in a small plant.

Previous work suggests therefore that the fundamental factors in the production of carbon black are the shape and size of the flame and the position occupied by the depositing surface. The shape and size of the flame depend on (a) the composition of the gas, (b) the pressure of the gas, (c) the design and dimensions of the burner, and (d) the composition and temperature of the atmosphere surrounding the flame. With the exception of (d) these variables are, in a given apparatus, under the control of the operator. The atmospheric conditions surrounding the flame are dependent on the geometry of

the apparatus, the number and arrangement of the burners, and the control of draft. With the exception of draft these factors are fixed at any time, hence the important variables to be examined are the channel height and draft control.

The conditions existing in a small plant are so different from those of large-scale operations that it might be thought that no common relations could be found. It will be shown presently, however, that in the laboratory there may be produced carbon blacks that closely resemble the commercial samples, hence it seems that the fundamental processes must be identical.

Description of Apparatus

Experimental

The burner chamber consisted of a sheet iron box bolted to a light iron frame, the dimensions being: length $37\frac{1}{2}$ in.; width, 14 in.; height, 28 in. The upper portion sloped inwards and terminated in two flues, which were spaced in such a manner as to obtain even removal of waste gases.

The channel was a 24 in. length of standard 6 in. structural steel. The large face was planed to obtain a smooth surface for the efficient operation of scrapers. This member was mounted on rails placed in the upper part of the chamber, and was given a reciprocating motion by a special reversing mechanism operated with an electric motor. Reversal took place every 1.5 min., resulting in a channel speed of 4.5 ft. per min.

The temperature of the burner chamber was obtained by inserting a thermometer into the space over the channel. The temperature of the channel itself was determined by means of a thermocouple which was peened (3) into its upper side and connected to the recorder by flexible leads which passed through suitable insulators in the side of the chamber. In certain experiments a thermocouple was placed inside one of the burner tips.

In order to ensure complete removal of carbon from the depositing surface, three scrapers were provided, each consisting of thin blades of spring steel which were pressed against the channel by suitable springs. The scrapers employed in the initial experiments were single blades, but these were later replaced by composite members consisting of three independent blades, each covering a third of the width of the channel with suitable overlaps.

The burners were carried on a 1 in. pipe placed parallel to and underneath the centre of the channel. From one to four burner tips were carried on this pipe, each being situated on a short riser. The adjustment of channel height was accomplished by changing the position of the burner pipe. Burner tips of the "Cabot" type were employed exclusively. This tip, which throws a flat flame similar to that employed in the early days of gas illumination, is stated to be employed more than any other type in the production of rubber blacks. The dimensions and shape of the burner tip are undoubtedly factors of prime importance in the production of carbon black, but in spite of the infinite number of variations which are possible, relatively few types are

employed. A comprehensive examination of this factor alone would provide material for an independent research, hence it seemed desirable to confine attention to one type only.

Control of draft was effected by suitable adjustment of two gate valves which were fitted to the outlets at the top of the burner chamber. In the results which follow, the setting of these valves is listed as the percentage of the full open position which existed during the experiment in question. These are arbitrary values which are of significance only to this particular apparatus. A more general indication of the draft conditions is given by analysis of the flue gases. Apertures were placed at the bottom of the chamber to admit the air necessary for combustion. While these were also fitted with adjustable covers, it was found more convenient to operate with constant settings and to control the draft solely by adjustment of the upper valves.

A constant flow of gas was supplied to the burners by the use of a flow-meter and suitable valves. The total amount of gas consumed during a given experiment was measured with a wet gasmeter. The carbon black falling from the scrapers was collected in a hopper from which it was removed for weighing at the termination of an experiment. Yields have been expressed in pounds per 1000 cu. ft., according to the usual practice, the volumes referring to a temperature of 22° C. and 760 mm. of mercury.

Experimental Results

Gas

The natural gas was obtained from the separators of a representative well in the Turner Valley, Alberta, and consisted of approximately 94% methane, the residue being largely ethane with small amounts of higher hydrocarbons. The value of n in $C_n H_{2n+2}$ was 1.13. It is important to note that any hydrogen sulphide originally present had been removed during the compression of the gas into cylinders, and subsequent transportation from the field to the laboratory. In later experiments, carried out to determine the effect of hydrogen sulphide on the yield and properties of the carbon, it was therefore necessary to add this impurity in the required proportions.

Effect of Channel Height on Yield

The result of altering the distance from the depositing surface to the tip is shown in Table I. With this particular tip and gas rate, the yield rises to a maximum at 1.75 in., falling off as greater distances are involved, as shown in Fig. 1. This behavior is characteristic of the impingement process and has been referred to by previous authors.

The yields that are obtainable from Turner Valley gas are very similar to those in commercial practice when a gas of this carbon content is employed. Of the members of the paraffin series, methane gives the poorest yield, as might be expected from its low heat of combustion and the refractory nature of the molecule. Very substantial improvements in yield are brought about by the addition of relatively small amounts of the higher homologues.

TABLE I
RELATION BETWEEN CHANNEL HEIGHT AND YIELD

Experiment	1	2	3	4	5	6	7	8
Burner, in.	0.010	0.010	0.010	0.010	0.010	0.012	0.012	0.012
No. and arrangement	2 at 4 in.	2 at 4 in.	2 at 4 in.	2 at 4 in.	2 at 4 in.	4 at 3.5 in.	4 at 3.5 in.	4 at 3.5 in.
Draft control	100	100	100	100	100	38	38	38
Gas rate, cu. ft./hr./tip	2.5	2.5	2.5	2.5	2.5	2.7	2.7	2.7
Channel temp., °C.	340	350	325	325	315	420	420	420
Channel height, in.	1.25	1.50	1.75	2.00	2.25	1.50	1.75	2.00
Yield, lb./1000 cu. ft.	0.7	1.2	1.3	0.9	0.3	1.2	1.2	0.9
Plant temp., °C.	—	—	—	—	—	153	152	138
Tip temp., °C.	—	—	—	—	—	237	240	227
Flue gas								
O ₂	—	—	—	—	—	19.3	18.0	18.3
CO ₂	—	—	—	—	—	1.9	1.3	1.3

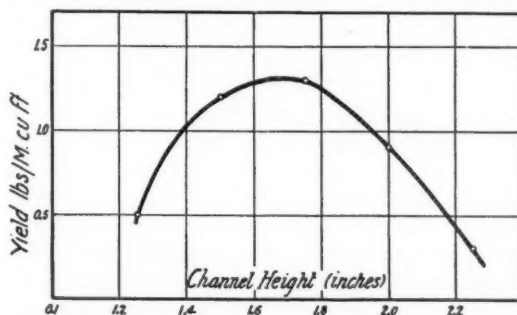


FIG. 1. Effect of channel height on yield of carbon black obtainable from Turner Valley gas.

Since the maximum yield is obtained when the channel is at some specific position in the flame, the position for this maximum will obviously depend on the gas pressure, which governs the height of the flame. Hence for every setting there will be a different position for maximum yield. The results of Drogin suggest that the actual magnitude of the maximum yield is approximately the same at different gas pressures as long as the shape of the flame remains unaltered. Thus at very low rates of flow the flame becomes nearly cylindrical, while at very high rates turbulence occurs; in both cases the relation breaks down. The channel temperatures holding in these experiments are considerably lower than those which are found in commercial plants where the proximity of many burners and adjacent channels raises the temperature almost 100° C. above the values appearing in Table I. It is to be noted also that the channel temperature changes in a regular manner with channel height. These differences are of some significance in controlling the properties of the carbon, as the amount of tars and similar products of incomplete combustion sorbed on the black are to some extent dependent on the temperature of the channel. These carbons do not appear to have suffered by the low channel temperature at which they were produced, as will be seen in a later section.

Effect of Draft Control

While frequent references to the important effects of "drafting" in the industry have been encountered, a definite relation between this factor, and the yield and properties of the carbon is lacking. Francis (4) has pointed out that, from a theoretical point of view, attempts to improve yield by stifling the flame are useless. Plummer and Keller (7) carefully controlled the air-gas ratio by metering the air as well as the gas supplied to the burners. Even this very commendable procedure failed to yield definite results, as these authors could notice "surprisingly little difference attributable to the combustion ratio".

In the present author's opinion, the chief use of draft restriction is the steadying effect which it exerts on the flames. One of the difficulties which beset this type of research lies in the fact that a luminous flame frequently develops a pulsation which prevents it from playing steadily on the channel. This phenomenon has been observed and commented upon by others (2, 4), and it has been concluded that it is caused by the flame velocity momentarily becoming greater than the gas velocity, so that the flame front advances to the burner tip where it is extinguished by the over-rich mixture in this vicinity. Whatever may be the cause, it is certain that this disturbance affects the yield unfavorably and makes the duplication of results difficult.

In some experiments the flames burned steadily, while at other times, without ascertainable cause, flickering would appear. It was found in all cases that the flames tended to burn more steadily when the draft was restricted. In addition to the pulsating flame, a more simple type of disturbance was observed. This was caused by convection currents which were set up when the draft through the apparatus was excessive. When either of these conditions obtained, the effective channel height was not constant, and, as shown previously, this factor exerts a profound effect on the recovery of carbon.

These observations are borne out in the results presented in Table II. In Experiments 9 to 14 only two burners were used. Under these circumstances the flames burned very steadily even with the drafts in the open position, owing to the fact that the burners did not set up convection currents of sufficient magnitude to interfere with each other. Restriction of draft, while it produced significant changes in the composition of the flue gas, did not affect the yield until the drafts were closed to 7% of the open position. At this point the luminosity of the flames was greatly reduced, the flame frequently burning at a distance from the tip. Under such conditions the yield is adversely affected.

In Experiments 15 to 18 a larger number of tips were employed with the result that, with the drafts in the open position, the flames were seriously disturbed by convection currents. The yield under these circumstances was considerably reduced. When the drafts were partly closed the condition was corrected and an improvement in yield followed. The final result was not, however, better than that obtainable with full draft when the flames burned steadily.

TABLE II
EFFECT OF DRAFT CONTROL ON YIELD (CHANNEL HEIGHT 1.75 IN.)

Experiment	9	10	11	12	13	14	15	16	17	18
Burner, in.	0.010	0.010	0.010	0.010	0.010	0.010	0.012	0.012	0.012	0.012
Channel temp., °C.	325	325	350	350	350	365	425	430	430	445
Plant temp., °C.	—	—	—	—	—	—	128	133	152	185
Tip temp., °C.	—	—	—	—	—	—	200	225	240	265
Gas rate, cu. ft./hr./tip	2.5	2.5	2.5	2.5	2.5	2.5	2.7	2.7	2.7	2.7
Draft aperture	100	80	50	28	21	7	100	50	38	21
Yield	1.2	1.18	1.16	1.26	1.25	—	0.92	1.18	1.24	1.36
Flue gas										
O ₂	20.0	19.2	18.3	18.0	17.7	17.0	20.1	19.5	18.0	16.0
CO ₂	0.4	0.5	0.8	1.0	1.7	1.7	0.3	0.6	1.3	1.9

There are other circumstances in which draft control would have more noticeable effects. When the air supply to a flame burning in secondary air is reduced, the flame becomes taller and narrower. This phenomenon brings about some of the effect of reducing the channel height. Thus by examining the effect of draft control at the channel height corresponding to the maximum yield, a point has been chosen at which the least effect would be noticed. Had a very high channel height been selected, restriction of draft would undoubtedly have produced a very pronounced effect. Such exceptional conditions are, however, seldom encountered in practice.

Effect of Hydrogen Sulphide in Gas

While it is unanimously agreed that the presence of appreciable amounts of sulphur in the gas results in corrosion of the plant and continuous trouble from clogging of burner tips, there has been some doubt as to the actual effect of this impurity on the carbon itself. In order to examine this point the apparatus was altered by the addition of a second flowmeter and gas volume measuring apparatus, so fitted that known amounts of hydrogen sulphide could be added to the methane. A specially designed baffled tube was interposed in the gas line before the burner pipe, to ensure complete mixing of the gases. The experiments involving the addition of hydrogen sulphide were not carried out with Turner Valley gas. A similar natural gas of the following constitution was employed: methane, 85; ethane, 13.5; nitrogen, 1.5%. In these experiments an 8 in. channel was employed upon which the carbon was deposited from two 0.022 in. Cabot tips. The yields under these circumstances were considerably lower than those that had been obtained with Turner Valley gas.

TABLE III
EFFECT OF HYDROGEN SULPHIDE ON YIELD
Cabot 0.022 in. Gas rate, 4.6 cu. ft./hr. Channel height, 2.25 in.

Experiment	19	20	21	22	23
Hydrogen sulphide, % by vol.	0.0	0.9	1.4	1.9	2.2
Yield, lb./1000 cu. ft.	1.0	0.9	0.8	0.9	0.8

The results of experiments with hydrogen sulphide are shown in Table III, from which it is evident that a slight reduction in yield follows the addition of this gas to the hydrocarbon. The change, however, is not greater than that which would follow the addition of any non-hydrocarbon to the methane, which is rather sensitive to such treatment owing to the reluctance with which it decomposes compared with higher members of the paraffin series. Since the average hydrogen sulphide content of Turner Valley gas is stated to be of the order of 1% by volume, the natural gas should not behave in a manner different from that of the synthetic mixtures employed in this research.

SOME PROPERTIES OF CARBON BLACK PRODUCED FROM TURNER VALLEY NATURAL GAS

Extractable Matter

It is well known that carbon black is not pure carbon, but contains appreciable amounts of adsorbed gases and compounds of tar-like nature (6), which may be driven off by heating to high temperatures or partly removed by extraction with suitable solvents. Goodwin and Park (5), using benzene and xylene, found that the extraction was not complete for several days. In the present research a hot extraction method was employed using successively, benzene, acetone, and chloroform, the latter solvent appearing to be particularly suitable for the extractables present in carbon black. The samples were placed in an A.S.T.M. apparatus for rubber extraction immersed in the boiling vapor of each solvent in turn, in such a manner that the condensed liquid remained on the black for various intervals. The samples were heated to 105° C. before and after extraction and the loss in weight measured.

With this method, larger amounts of extractable matter were recorded after three hours' extraction than those obtained by Goodwin and Park at the end of four days. This difference may be due either to the samples or to the efficacy of the solvents. In the present work only comparative results were required, hence this discrepancy has not been examined exhaustively. The results of a number of determinations are shown in Table IV. Samples *A*, *B* and *C* were standard commercial rubber blacks, Sample *C*, being of the "dustless" variety, having been subjected to a patented treatment resulting in the production of pellets.

TABLE IV
EXTRACTABLE MATTER IN CARBON BLACK

Sample	20	21	15	19	1% H ₂ S	<i>A</i>	<i>B</i>	<i>C</i>
Channel height, in.	1.25	1.50	1.75	2.00	1.75	?	?	?
Extractable, %	1.8	0.0	0.4	0.8	0.7	1.2	0.6	2.2

The amount of extractable matter in the experimental blacks is not greater than that found in the standard commercial rubber blacks. It is also interesting to observe indications of a relation between channel height and the amount of extractable. The value is highest with low channel heights, falling

to zero in the region of maximum yield and rising again with the highest channel distances. This relation follows the yield and also the temperature of the channel. It may be suggested, therefore, that the amount of extractable material that may be occluded in the carbon will depend on the temperature of the channel.

Sorption

The sorptive capacity of a carbon black is stated to bear a relation to its vulcanization characteristics in rubber. This property has been examined using methylene blue, which was chosen because of the convenience with which the measurements may be carried out.

The standard procedure that has been followed was described in the previous paper in this series. Results obtained with various samples are given in Table V.

TABLE V
SORPTION OF METHYLENE BLUE BY CARBON BLACK

Sample	Hubers airfloated	B & S uncompressed	15 (optimum yield)	1.4% H ₂ S	2.2% H ₂ S	3.2% H ₂ S
Sorption, mg./gm.	32.0	38.8	37.5	36.0	34.8	34.8

NOTE.—Carbon black (0.25 gm.) shaken with 50 cc. of 0.025% aqueous methylene blue solution.

The sorptive power of these carbon blacks is of the same order as that of the commercial rubber type, so that similar vulcanization behavior in rubber would be expected. A detailed discussion of the effect of channel height and other variables on the sorptive properties of the carbon will be reserved for a later paper.

The sorption of methylene blue by samples produced from a sulphur-containing gas is also shown in Table V, in which it will be seen that a very slight reduction in the amount of sorption is produced, but such differences in sorption are not greater than the error of this test as applied to the vulcanization characteristics of the carbon.

So far as may be ascertained from these tests, there is no reason why these blacks should not exhibit good properties in rubber.

REINFORCEMENT OF RUBBER

In view of the low yields that are an unavoidable consequence of the channel process, it was impossible to obtain a sufficient amount of carbon to carry out full-scale rubber tests in all cases. A special experiment was therefore performed under conditions productive of the optimum yield. The resulting sample was tested in rubber according to the formula and method described in the previous paper of this series. The results shown in Table VI indicate that the experimental blacks are considerably superior to the commercial blacks that were examined concurrently. It is assumed that this superiority

TABLE VI
TENSILE PROPERTIES

Cure, min.	Modulus at elongation of					Ultimate tensile	Ultimate elonga- tion
	100%	200%	300%	400%	500%		
Experimental carbon blacks*							
45	11.6	26.4	48.5	98.3	156	239	601
60	14.5	34.7	70.3	117	178	223	574
75	16.0	40.8	80.4	131.2	185.8	244.4	540
Cabot's "Spheron"							
45	10.8	22.8	46.7	88.8	127	168	573
60	12.8	30.9	62.7	107.2	162.5	180	532
75	13.2	33.8	66.8	113.8	171.5	192.2	541
B & S Uncompressed							
45	7.9	18.5	39.6	71.8	114.7	172	608
60	9.5	18.8	42.1	81.8	128.1	194	604
75	11.6	28.6	58.7	100	158	181	596

*Cabot 0.012 in. 4 at 4 in. Gas rate, 2.76 cu. ft./hr./tip. Upper drafts, 21%. Channel height, 1.75 in. Channel temperature, 450° C. Yield, 1.25 lb./1000 cu. ft.

is not due to any virtue resident in the gas itself, but rather to the superior control and freedom from impurities which, in the small apparatus, result in the production of a black that could be imitated only with difficulty in full-scale practice. (All the values in this particular test were much lower than those commonly obtained with this formula, perhaps owing to some peculiarity of the rubber bale. The results are considered to have only comparative value.) The quantities of carbon obtained from gases containing sulphur were insufficient to carry out full-scale rubber tests. A few small samples obtained from gas containing 1% of hydrogen sulphide were vulcanized in a special ring mold described by Stedman (8); no difference attributable to the presence of sulphur could be detected.

Conclusion

It has been shown that a carbon black possessing good properties may be produced from Turner Valley gas with yields of 1.3 lb./1000 cu. ft. Hydrogen sulphide has been added to natural gas in amounts as high as 3% by volume without bringing about appreciable changes in the amount of extractable matter or sorptive properties of the carbon. Only a few rubber tests of samples produced from sulphur-containing gas were carried out, and, while the fact was not definitely established, it seems that, with the additional evidence from extraction and sorption measurements, the carbon black produced from this gas is identical with that obtainable from a sulphur-free gas.

It must be understood, however, that there are a number of factors involving the time scale that are not operative in a small plant. The presence of hydrogen sulphide undoubtedly accelerates corrosion in elaborate systems of pipe work which constitute a commercial plant. After operation for some time with such a gas, the possibility of iron sulphides and other sulphides flaking off and being collected with the carbon black introduces a factor that was not present in these experiments. Many of the inferior properties that have been associated with carbon blacks produced from gases high in sulphur constitute probably a secondary effect caused by the degeneration of the plant under the destructive action of this gas.

Owing to restrictive legislation, the carbon black producers in the state of Texas, U.S.A., are now required to employ sulphur-containing gases exclusively. It is understood that higher concentrations than had heretofore been considered possible are being successfully employed.

After removal of hydrogen sulphide, the Turner Valley gas produced a carbon black that is very similar to those appearing on the market and in general use by the rubber industry.

Acknowledgments

The author wishes to acknowledge his indebtedness to Mr. C. Girard who prepared a number of the carbon black samples, to Mr. T. Griffith who carried out the rubber tests, and to Dr. G. S. Whitby, Director of the Division of Chemistry, at whose suggestion this investigation was carried out.

Thanks are also due to the American Lava Corporation of Chattanooga, Tenn., U.S.A., for the Lava tips used in this work.

References

1. CHAMBERLIN, D. S. and ROSE, A. *Trans. Am. Inst. Chem. Eng.* 22 : 155-164. 1929.
2. CHAMBERLIN, D. S. and THRUN, W. E. *Ind. Eng. Chem.* 19 : 752-754. 1927.
3. DROGIN, I. *India Rubber J.* 90 : 259-274. 1935.
4. FRANCIS, A. W. *Ind. Eng. Chem.* 23 : 612-617. 1931.
5. GOODWIN, N. and PARK, C. R. *Ind. Eng. Chem.* 20 : 621-627. 1928.
6. NEAL, R. O. and PERROTT, G. St. J. *Bur. Mines Bull.* 192. 1922.
7. PLUMMER, W. B. and KELLER, T. P. *Ind. Eng. Chem.* 22 : 1209-1211. 1930.
8. STEDMAN, D. F. *Can. J. Research*, 6 : 518-520. 1932.
9. WIEGAND, H. B. *Ind. Eng. Chem.* 23 : 178-181. 1931.



